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In the Supreme Court of the United States

OCTOBER TERM, 1971.

No. 71-671

WESTWOOD CHEMICAL, INC.,

Petitioner,

v.

OWENS-CORNING FIBERGLAS CORPORATION,

Respondent.

PETITION FOR A WRIT OF CERTIORARI
To the United States Court of Appeals
For the Sixth Circuit.

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WESTWOOD CHEMICAL, INC.,

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OWENS-CORNING FIBERGLAS CORPORATION

Respondent.

PETITION FOR A WRIT OF CERTIORARI
To the United States Court of Appeals For the Sixth Circuit.

Westwood Chemical, Inc., the petitioner herein, prays that a writ of certiorari issue to review the judgment of the United States Court of Appeals for the Sixth Circuit entered in the above cause on August 24, 1971.

OPINIONS BELOW.

The opinion of the United States Court of Appeals for the Sixth Circuit, not yet reported, is reprinted in Appendix A. The judgment of the Court of Appeals in the Sixth Circuit is reprinted as Appendix B. The Order of the Sixth Circuit denying rehearing is reprinted as Appendix C. The Findings of Fact and Conclusions of Law of the United States District Court for the Northern District of Ohio, Eastern Division, filed on July 30, 1970, and reported at 317 F. Supp. 201, is reprinted in Appendix D. The patents in controversy are included as a ready reference for the convenience of the Court as Appendix E.

JURISDICTION.

The judgment of the United States Court of Appeals for the Sixth Circuit was entered on August 24, 1971. Petition for Rehearing was sought and rehearing was denied on October 19, 1971. The jurisdiction of this Court is invoked under 28 U.S.C. Sec. 1254(1).

QUESTIONS PRESENTED.

1. Under the patent laws of the United States, Title 35, U.S.C., is it error on review of a finding of obviousness under 35 U.S.C. Sec. 103 to vitiate the presumption of validity to which a patentee is otherwise entitled under 35 U.S.C. Sec. 282 by the teachings of a non-reference prior art patent when the exact wording of the so-called non-reference is contained in a reference patent which was considered by the patent examiner who thereafter determined patentability?

2. Is a finding by the trial judge sitting without jury that a so-called non-reference patent is "pertinent" prior art binding on the reviewing court as a binding finding of fact not clearly erroneous under the provisions of Federal Rule 52(a) F.R.C.P. even though the relied upon words of such so-called non-reference are contained in a reference which was considered by the patent examiner who thereafter determined patentability?

3. Does Rule 52(a) F.R.C.P. preclude review of the evidentiary basis of a finding by the trial judge sitting without jury in a patent infringement suit that a non-reference patent was pertinent prior art even though the record clearly demonstrates that every witness in the case, including Respondent's experts, admitted that the compound disclosed in the alleged pertinent prior art patent was of an entirely different class of chemicals from those

disclosed in the patent in suit and from those required to provide the advantages of the patent in suit?

4. Should Rule 52(a) F.R.C.P. be binding on the reviewing court so as to require it to affirm findings of fact and conclusions of law of the trial judge in a patent infringement case when the trial record demonstrates that the petitioner (patentee's assignee) was denied fair opportunity to produce rebuttal evidence to sustain validity of the patent and where cross-examination of alleged infringer's principal expert was unduly restricted?

STATUTES AND RULES INVOLVED.

35 U.S.C. Sec. 103:

A patent may not be obtained though the invention is not identically disclosed or described as set forth in section 102 of this title, if the differences between the subject matter sought to be patented and the prior art are such that the subject matter as a whole would have been obvious at the time the invention was made to a person having ordinary skill in the art to which said subject matter pertains. Patentability shall not be negatived by the manner in which the invention was made. (July 10, 1952, c. 950, sec. 1, 66 Stat. 798.)

35 U.S.C. Sec. 282:

A patent shall be presumed valid. Each claim of a patent (whether in independent or dependent form) shall be presumed valid independently of the validity of other claims; dependent claims shall be presumed valid even though dependent upon an invalid claim. The burden of establishing invalidity of a patent or any claim thereof shall rest on the party asserting it.

Federal Rules of Civil Procedure, Rule 52(a):

In all actions tried upon the facts without a jury or with an advisory jury, the court shall find the facts specially and state separately its conclusions of law thereon, and judgment shall be entered pursuant to Rule 58; and in granting or refusing interlocutory injunctions the court shall similarly set forth the findings of fact and conclusions of law which constitute the grounds of its action. Requests for findings are not necessary for purposes of review. Findings of fact shall not be set aside unless clearly erroneous, and due regard shall be given to the opportunity of the trial court to judge of the credibility of the witnesses. The findings of a master, to the extent that the court adopts them, shall be considered as the findings of the court. If an opinion or memorandum of decision is filed, it will be sufficient if the findings of fact and conclusions of law appear therein. Findings of fact and conclusions of law are unnecessary on decisions of motions under Rules 12 or 56 or any other motion except as provided in Rule 41(b).

STATEMENT OF THE CASE.

This action was brought on June 10, 1963, by petitioner, for alleged infringement of certain patents, reprinted in their entirety as Appendix E, of which it is the assignee, and known as patent Nos. 2,742,378 and 2,841,566. These are chemical process and product patents concerned with a product known as reinforced plastic and methods for manufacturing the same. Such plastics have substantial commercial application in the making of solid "composite articles," such for example as a fiberglass boat or fiberglass auto body. The two principal components of the end product are the plastic and the reinforcing materials. The latter may be either a form of textile fiber or powdered solids. The purpose of the reinforcing materials is to greatly increase the strength of the plastic thereby making the end product commercially practicable. The products and methods taught by the patents in controversy have strength and moisture resistant properties unknown in the prior art. Petitioner contends that Respondent appropriated for its unjust enrichment and commercial advantage the teachings of these patents without benefit of license not only to petitioner's detriment but the detriment of its licensee who had paid substantial moneys for the benefits of said license.[1]

Prior to the claimed inventions, it was well-known in the art that plastics, including resins and rubbers, would

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[1] The finding of invalidity of the patent is especially catastrophic to petitioner in this case because its licensee whose license petitioner was seeking to protect through the instant litigation has now itself refused further payment of royalty and is relying upon the decision of this Court in *Lear, Inc. v. Adkins*, 395 U.S. 653, 89 S. Ct. 1902 (1969) which permits licensee to now contest invalidity coupled with doctrine of *Blonder-Tongue Lab., Inc. v. University of Illinois Foundation*, 402 U.S. 313, 91 S. Ct. 1434 (1971) creating an estoppel to re-litigate validity of patents except on certain very narrow grounds of fair trial or whether the initial trial judge understood the invention.

be substantially strengthened by the use of reinforcing materials such as textile fibers and/or powdered solids. However, such reinforced plastic products suffered the detriment that the adhesion between the plastic and reinforcing material would strip or break down in the presence of moisture, either direct immersion or atmospheric, causing substantial loss of strength. This made it necessary for producers of such products to compensate by additional thickness, bulk and weight. Petitioner's assignor, the inventor herein, Theodore TeGrotenhuis, discovered that by the pretreatment of the reinforcing fibers or solids with a certain type of chemical, now-termed "coupling agent," that such reinforcing materials in turn could be chemically combined with the plastic in a single molecule possessing hitherto unknown qualities of strength and moisture resistance thereby making it possible to manufacture finished products able to withstand forces and stresses with significantly less weight and bulk than before required.[2] Prior to the discoveries of TeGrotenhuis which culminated in his patents, the cause of loss of strength under moisture-producing conditions of reinforced plastic products was unknown. TeGrotenhuis discovered that the cause was moisture accumulating on the surface of the reinforcing materials due to their particular surface chemical properties which would cause the reinforcing material to slip away from the plastic it was to reinforce causing a breakdown in strength. He further discovered that certain chemical compounds, reflected in the teachings of his patents, would act as a bonding or coupling agent between the reinforcing material and plastic so as to abrogate this problem and thereby main-

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[2] For a good description of the invention insofar as its technicalities are concerned, the Court is respectfully referred to the interference proceeding of *TeGrotenhuis v. Yaeger*, 290 F.2d 951 (1961), especially p. 952.

tain reinforcement at full strength. T. Grotenhuis assigned the patents with these teachings to petitioner on September 29, 1961.

Respondent is a major producer of glass fiber reinforcing material and other reinforced plastic products. The lawsuit sought a decree of infringement relative to the above two stated patents against respondent by reason of the fact that respondent manufactured, sold and used reinforced plastic products which appropriated the teachings of the aforesaid patents without payment of royalty. The case was tried to the district judge, non-jury, who thereupon entered judgment on July 29, 1970. The findings of fact and conclusions of law of the trial judge in substance rejected all of petitioner's claims of infringement and further, in accordance with the affirmative defenses of respondent, found the patents themselves invalid. Appeal was thereupon perfected to the United States Court of Appeals for the Sixth Circuit. That court focused its decision on the issue of invalidity of the patents by reason of the affirmative defense of obviousness as spelled out in 35 U.S.C. Sec. 103. The reviewing court took the position that the findings of fact and conclusions of law of the trial judge relative to the affirmative defense of obviousness (35 U.S.C. Sec. 103) were not clearly erroneous in the court below within the meaning of Rule 52(a) F.R.C.P. The evidentiary basis relied upon was that certain alleged pertinent prior art references not before the patent examiner vitiated any presumption of validity of the patent (as to non-obviousness) to which petitioner would be otherwise entitled pursuant to the provisions of 35 U.S.C. Sec. 282.[3] Petitioner filed a petition

[3] The Sixth Circuit, like the Fifth Circuit, apparently has interpreted various decisions of this Court as meaning that at least on review the reviewing court should direct its attention

(Continued on following page)

for re-hearing with the United States Court of Appeals for the Sixth Circuit alternatively for re-hearing with the same court or en banc but same was denied October 19, 1971. Thus, the case now comes to this Court on petition for review for resolution of certain vital questions requiring pronouncement by this Court if the patent laws of the United States are to have uniform application throughout the circuits.

Petitioner contends that the effect of the reasoning reflected in the opinion and judgment of the United States Court of Appeals for the Sixth Circuit in the instant case is reflective of serious controversies in the various circuit courts of appeals and district courts which should give uniform application to the patent laws of the United States and the intent of Congress as enunciated in said laws of the standard of proof to vitiate the presumption of patentability under 35 U.S.C. Sec. 282. Petitioner further claims that the questions raised by the instant petition are unsettled and are of great significance and magnitude in the field of patent law particularly because of the ever-growing trend due to the complexities of this kind of litigation to rely upon non-jury trials thereby giving added impetus to the applicability of Rule 52(a) F.R.C.P. to patent litigation.

One always hesitates in seeking certiorari to this Court to raise an issue of fundamental trial procedure and the fairness of the trial before the district judge. In this case, as will be noted in discussion under question 4, *infra*, the refusal of the trial judge to permit petitioner full

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(*Continued from preceding page*)

to the issue of validity of the patent and if this issue is decided against the patentee this disposes of the case on review. See *Beckman Instruments, Inc. v. Chemtronics, Inc.*, 439 F.2d 1369 (5th Cir. 1970). Thus the Sixth Circuit having found the trial judge's finding of obviousness not to be clearly erroneous disposed of the case on this narrow ground.

scope of rebuttal testimony and cross-examination of respondent's expert raises an additional fundamental question particularly incident to patent litigation in view of this Court's pronouncement of estoppel to re-litigate patent validity against subsequent infringers.

REASONS FOR GRANTING THE WRIT.

Because of the novelty and importance of the questions presented relating to the interpretation of the patent laws of the United States, petitioner begs the indulgence of the Court in permitting a brief discussion as to the reasons why each of said questions on which review is sought merits consideration and decision by this Honorable Court.

1. Under the patent laws of the United States, Title 35, U.S.C., is it error on review of a finding of obviousness under 35 U.S.C. Sec. 103 to vitiate the presumption of validity to which a patentee is otherwise entitled under 35 U.S.C. Sec. 282 by the teachings of a non-reference prior art patent when the exact wording of the so-called non-reference is contained in a reference patent which was considered by the patent examiner who thereafter determined patentability?

A reading of the opinion and judgment of the Sixth Circuit makes it clear that that court agreed that the trial judge's finding that three so-called non-reference prior art patents were "pertinent" and therefore vitiated the presumption of validity (non-obviousness) to which petitioner is otherwise entitled under the plain provisions of Title 35 U.S.C. Sec. 282 was not clearly erroneous. Two of these non-reference patents are referred to in the record (and the opinion of the reviewing Sixth Circuit Court of Appeals) as the Biefeld Patent No. 2,392,805

and the Hyde Patent No. 2,390,370. The record before the court clearly established that the *exact language* of these so-called non-reference prior art patents (Biefeld and Hyde) *was contained in two reference patents.*[1] Never before the present decision for review has a circuit court of appeals held that wording in a non-reference

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[1] The language in *Biefeld* and *Hyde* contended to be a pertinent prior art non-reference is the following:

> "By hydrolyzable organo-silicanes or silanes is meant derivatives of SiH_4 which contains readily hydrolyzable radicals such as halogens, amino groups, alkoxy, aroxy, and acyloxy radicals, etc. and organic radicals that are joined to the silicon atoms through carbon atoms. Examples of such organic radicals are as follows: aliphatic radicals, such as methyl, ethyl, propyl, isopropyl, butyl, amyl, hexyl, heptyl to octadecyl and higher; alicyclic radicals, such as cyclopentyl, coclohexyl, etc., aryl and alkaryl radicals such as phenyl, momo- and poly-alkyl phenyls as tolyl, xylyl, mesityl, mono-, di-, and tri-ethyl phenyls, mono-, di-, and tripropyl phenyls, etc.; naphthyl, mono- and poly-alkyl naphthyls as methyl naphthyl, diethyl naphthyl, tri-propyl naphthyl, etc.; tetrahydro-naphthyl, anthracyl, etc.; aralkyl such as benzyl, phenyl-ethyl, etc.; *alkenyl such as methallyl, allyl, etc.;* and hetrocyclic radicals. The above organic radicals may also, if desired, contain inorganic substituents such as halogens, etc." (Emphasis ours.)

This language appears in column 1, lines 19-39, p. 2 of the Biefeld patent 2,392,805; also on p. 2, column 1, lines 43-63 of Hyde patent 2,390,370. However, this same language also appears in line 54, column 1 to line 22, column 2 of Johannson patent 2,436,304, a patent office reference; also, it appears verbatim in line 44, column 1 to line 13, column 2 of Johannson patent 2,557,786 also a patent office reference.

The quoted paragraph of *Biefeld* and *Hyde* from the record evidence is the only portion of *Biefeld* and *Hyde* that was relied upon as pertinent prior art and for some reason the significance of this exact language being in reference patents completely eluded both the trial court and the Sixth Circuit.

The vague reference in the above language of *Biefeld* and *Hyde* to alkenyl compounds as constituting a "pertinent" teaching is also directly contrary to a long line of contrary decisions: *Hanes Stellite Company vs. Chesterfield,* 22 F.2d 635, 637 (6th Circuit 1927); *Fulton Company vs. Bishop & Babcock,* 284 Fed. 774, 777 (6th Circuit, 1922); *Tilghman vs. Proctor,* 102 U.S. 707, 771 (1881); and *E. I. DuPont de Nemours vs. Ladd,* 328 F.2d 547, 549, 551 (D.C. Cir., 1964).

to the patent should be given weight on a defense of obviousness under 35 U.S.C. Sec. 103 to vitiate the presumption of validity (which includes non-obviousness) under 35 U.S.C. Sec. 282 when the exact wording of the so-called non-reference is contained in a reference patent considered by the patent examiner to be the most pertinent prior art.[*]

When the language in a non-reference is contained in a reference considered and rejected by the patent examiner who thereafter allows the claims, patent law heretofore has always been settled that this consideration of language by the patent examiner *strengthens* rather than *vitiates* the presumption of validity. The doctrine is usually expressed on the principle that where the best of art relied upon by the alleged infringer was before the patent office when it granted the patent, said facts strengthen the presumption of validity of the patent. See *Cold Metal Process Company v. Republic Steel Corp.*, 233 F.2d 828 (6th Cir. 1956); *Tabco Products Company v. Van Mark Products Corp.*, 446 F.2d 420 (6th Cir. 1971); *LaSalle Street Press v. McCormick & Anderson, Inc.*, 445 F.2d 84 (7th Cir. 1971); and cases cited therein.

The language of *Otto v. Koppers Company*, 246 F.2d 789, 801 (7th Cir. 1957), *cert. den.* 355 U.S. 939, is particularly significant:

"Astute and enterprising attorneys can always find references not of record in the Patent Office, but if

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[*] In fact, three different sets of patent examiners in different patent office chemical divisions independently allowed claims of the two patents in this litigation over all references, once in Serial No. 243,737; once in Serial No. 302,415 which matured into Patent No. 2,742,378 a patent in suit; and once in Serial No. 439,463 which matured into Patent No. 2,841,566 the other patent in suit. In addition, Patent No. 2,742,378 withstood a hotly contested interference proceeding ultimately reported as *TeGrotenhuis v. Yaeger*, 290 F.2d 951 (1961).

> they do not involve some substantial element in the defense of anticipation which was not considered by the Patent Office, the failure to make them record references cannot weaken the statutory presumption."

It is particularly onerous that the strong presumption intended by Congress to sustain the validity of the patent as spelled out in 35 U.S.C. Sec. 282 should be permitted to be overturned by a non-reference when the identical language was contained in a reference and the patent itself was subsequently sustained in a hotly contested interference proceeding in the patent office. The Sixth Circuit in the instant case erred in using the language of the Hyde and Biefeld patents as alleged "pertinent" prior art to vitiate the presumption of validity as to non-obviousness, and compounded the error by failing to give any cognizance to the interference proceeding to which the patent claims had been subjected. This Court should make it clear that language in a non-reference, when said language has already been reviewed by the patent examiner in a prior art patent believed by the examiner to be the most pertinent prior art, should *strengthen*, not *weaken* the presumption of validity both on the issues of anticipation and non-obviousness. This error by the Sixth Circuit has the effect of vitiating opinions of long standing in patent law by this Court as reflected in *Hildreth v. Mastoras*, 257 U.S. 27 (1921); *Radio Corporation of America, et al. v. Radio Engineering Laboratories, Inc.*, 293 U.S. 1 (1934) which placed great emphasis on the effect of an interference proceeding in the patent office.

2. Is a finding by the trial judge sitting without jury that a so-called non-reference patent is "pertinent" prior art binding on the reviewing court as a binding finding of fact not clearly erroneous under the provisions of Federal Rule 52(a) F.R.C.P. even though the relied upon words of such so-called non-reference is contained in a reference which was considered by the patent examiner who thereafter determined patentability?

With regard to the same two so-called non-reference prior art patents (Biefeld and Hyde), the Sixth Circuit opinion reflects that that court felt itself bound to affirm the conclusion of the trial court below as not being clearly erroneous on the basis of Rule 52(a) F.R.C.P. It goes without saying that if there is a sufficiency of proof that a non-reference is "pertinent" prior art not before the patent office such pertinent prior art does and should weaken the presumption of validity. Whether or not such prior art is in fact "pertinent" must be a question of fact. The dilemma before the Court is the scope of review of sufficiency of the evidence to meet a *uniform* standard of proof in all the Circuits under Rule 52(a) F.R.C.P. as applied to patent cases. Is the burden of proof of the alleged infringer to prove the "pertinency" of the prior art by clear and convincing evidence? *Radio Corporation of America, et al. v. Radio Engineering Laboratories, Inc.*, 293 U.S. 1 (1934); *Universal Meriam Corp. v. Warner & Swasey Co.*, 354 F.2d 541 (1965), *cert. den.* 384 U.S. 927; *King-Sealy Thermos Co. v. Tastee Freeze Industries, Inc.*, 357 F.2d 875 (1966), *cert. den.* 385 U.S. 817; *Copease Mfg. Co. v. American Photocopy Equipment Co.*, 298 F.2d 772 (1961). The confusion in the circuits on this vital issue is clearly spelled out by footnote of *Woodstream Corp. v. Herter's Inc.*, 446 F.2d 1143 (8th Cir. 1971):

"* * *

"Courts have differed as to the quantum of proof required to overcome the presumption of patent validity. See L & A Products, Inc. v. Britt Tech Corporation, 365 F.2d 83, 86 (8th Cir. 1966) ("substantial evidence"); Ever-Wear, Inc. v. Wieboldt Stores, Inc., 427 F.2d 373, 375 (7th Cir. 1970) ("clear and cogent evidence"); Purer & Company v. Aktiebolaget Addo, 410 F.2d 871, 879 (9th Cir.), cert. denied, 396 U.S. 834, 90 S.Ct. 90, 24 L.Ed.2d 84 (1969) ("clear and convincing proof"); Foster Cathead Company v. Hasha, 382 F.2d 761, 764 (5th Cir. 1967) cert. denied, 390 U.S. 906, 88 S.Ct. 819, 19 L.Ed.2d 872 (1968) ("any reasonable doubt"). More recently, the Fifth Circuit applied the "clear and convincing evidence" standard in Stamicarbon, N. V. v. Escambia Chemical Corporation, 430 F.2d 920, 924 (5th Cir.) cert. denied, 400 U.S. 944, 91 S.Ct. 245, 27 L.Ed.2d 248 (1970). *The court noted, however, that the authorities are in a morass of conflict on this issue, citing several of the standards employed. Id.* at 924-925." (Emphasis ours.)

In addition to the need for a clear pronouncement of standard of proof, there has never been a clear decision by this Court as to whether a finding of fact which might be sustained as not clearly erroneous on the grounds that it meets the standard of greater weight or preponderance of the evidence would nevertheless be clearly erroneous because it fails to meet the test of proof by clear and convincing evidence. For the sake of clarity and uniformity in the application of the patent laws and particularly the construction of 35 U.S.C. Sec. 282, this Court should review this case as a vehicle to pronounce that a finding of "pertinency" of an alleged prior art non-reference does not satisfy the clear and convincing evidence test which shall be required to vitiate the presumption of validity under 35 U.S.C. Sec. 282 when the same language was

before the patent office in a reference patent and the patent issued. Such pronouncement would then serve as a beacon light to all courts below as to how to properly apply the "clearly erroneous" standard under Rule 52(a) F.R.C.P. on a finding of invalidity bottomed upon alleged non-reference prior art.

It has, of course, long been the position of this Court that great weight is to be given the decision of administrative agencies possessing particular expertise in the field involved which expertise is not to be upset in judicial proceedings absent abuse of discretion. One would certainly think that the particular expertise of chemical examiners should be accorded this weight particularly when there was also a hotly contested interference proceeding. See, for example, *Higley v. Brenner*, 387 F.2d 855 (1967); *Armstrong v. Motorola, Inc.*, 374 F.2d 764 (1967); Note 25, "Federal Practice and Procedure," 1970 Supplement, Volume 2B, p. 191.

3. Does Rule 52(a) F.R.C.P. preclude review of the evidentiary basis of a finding by the trial judge sitting without jury in a patent infringement suit that a non-reference patent was pertinent prior art even though the record clearly demonstrates that every witness in the case, including Respondent's experts, admitted that the compound disclosed in the alleged pertinent prior art patent was of an entirely different class of chemicals from those disclosed in the patent in suit and from those required to provide the advantages of the patent in suit?

Petitioner does not claim (as he does with reference to the reliance on the Biefeld and Hyde patents) that the third patent given great weight by the Sixth Circuit opinion contained language considered by the patent examiner. However, as shall shortly be demonstrated, reliance on this patent is likewise misplaced by the record evidence.

This third patent is referred to in the record as the Steinman patent No. 2,513,268. Despite the great weight given this patent as pertinent prior art by the trial judge and the Sixth Circuit, there is not a shred of record evidence to indicate that this Steinman patent was ever urged upon the patent examiner as significant prior art by anyone. Furthermore, there is not a shred of evidence in the record to indicate that the patent examiner was not aware of the Steinman patent and discarded it as non-significant (which it is).* Indeed the evidence is all the

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* Defendants' expert Dr. Rockow (10:2032) admitted the allyl silicates to be an entirely different class of materials, from the vinyl and or allyl silanes required by the patents in suit. So did published material of Biefeld and Phillips PX. 158 (6:1044-1045). The allyl silicates of the Steinman '268 patent are so different from the vinyl and allyl silanes that Steinman in his later filed '288 patent (which would be pertinent if filed earlier), did not even make a reference to his '268 patent application or to allyl silicates. In '268 no reference was made to silanes (11:2343). The *same* examiner who had *both* the Steinman '288 and '268 patent applications before him at the same time, didn't refer to either or require cross-reference in either patent.

Compare PX-173 5:1060-1107 with DXQQ 8:1471-1553. Plaintiff never contended he could use any silicate. In his 1945 application and in all subsequent, Plaintiff stressed the importance of *one* non-hydrolizable direct carbon-to-silicon bond in his hydrolizable allyl and vinyl silanes.

In the allyl silicates of '268, all four groups are attached to silicon by a carbon-oxygen-silicon bond (also designated ester linkage) and all will hydrolize (split off) in a humid atmosphere. *Defendants' expert Biefeld (11:2127) and Defendants' expert Steinman (8:1588 and 11:2300, 2301, 2347), both admitted to this fact.* Moreover, the allyl silicates were merely added into the resin (Steinman 11:2340). Certainly these admissions by Defendants' own experts, clearly show that allyl silicates and allyl silanes operate in a very different manner, the Court's finding to the contrary notwithstanding. A temporary improvement occurs in the strength of composite articles having fiber treated by allyl silicate *when the articles are freshly made or maintained in a bone dry atmosphere and never subjected to any humidity*, but this disappears. Protection from a humid atmosphere is obviously not practical and silicates *were never used.* The only pertinence of '268 is that, it is conclusive proof that as of 12/31/44, Steinman did not have in mind an allyl silane. *Clark*

(Continued on following page)

other way. The record in fact shows applications maturing into Steinman Patent No. 2,513,268 and Patent No. 2,563,288, which latter was a reference to patents in suit were before the Examiner, D. Arnold, at the same time. (Compare Vol. 8, p. 1556 and Vol. 6, p. 1088 of Appendix before Sixth Circuit.)

The Sixth Circuit opinion by its great emphasis on the alleged importance of the Steinman patent (No. 2,513,268) amounts to upholding under the guise of Rule 52(a) F.R.C.P. a speculation by the trial court completely unsupported by the record evidence that the patent examiner was unaware of this Steinman patent. Of course the same standard of proof, i.e., proof by clear and convincing evidence should be imposed on the alleged infringer with regard to whether Steinman patent No. 2,513,268 was "pertinent" prior art not before the examiner. Thus, both the trial court and the Sixth Circuit failed to require the Respondent, the alleged infringer, to prove by clear and convincing evidence the two essentials required of the Steinman patent to vitiate the presumption of validity of non-obviousness to which petitioner was entitled under 35 U.S.C. Sec. 282. These two essentials are the following:

1. That the patent examiner was unaware of the Steinman patent.

2. That if the patent examiner were aware or had considered this patent in all common probability the patent in litigation would not have issued.

Neither of these fundamental two propositions was established by any evidence much less clear and convincing evidence.

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v. Camras, 204 F.2d 273 at 280. His first application of an allyl silane to fibers, was in July, 1945, much after TeGrotenhuis' effective filing date (11:2338-9).

It is particularly sad that the courts below placed emphasis on the Steinman patent when the record evidence clearly disclosed that every expert, plaintiff's and defendant's, agreed in the record that the chemical combinations of the Steinman patent cannot and do not function in the same way as the chemical combinations of the patent in suit nor do they teach or provide the moisture resistant properties (greatly increased wet strength) of the TeGrotenhuis combinations which are the substance of the invention!

Once again, this Court should shoulder the mantle of responsibility to construe Rule 52(a) F.R.C.P. to throw some light on the applicability of this rule to patent cases and require that a trial court, non-jury, must do more than merely weigh the credibility of experts to find obviousness or anticipation so as to invalidate an otherwise valid patent which has cleared the patent office if the requirement of clear and convincing proof of invalidity by the alleged infringer is to be the standard and have any real meaning.

4. Should Rule 52(a) F.R.C.P. be binding on the reviewing court so as to require it to affirm findings of fact and conclusions of law of the trial judge in a patent infringement case when the trial record demonstrates that the petitioner (patentee's assignee) was denied fair opportunity to produce rebuttal evidence to sustain validity of the patent and where cross-examination of alleged infringer's principal expert was unduly restricted?

Whether petitioner received a fair trial is of especial importance in patent litigation as a consequence of the pronouncement of this Court in *Blonder-Tongue Laboratories, Inc. v. University of Illinois Foundation*, 402 U.S. 313, 91 S. Ct. 1434 (1971). Indeed, in this very case, a proper

resolution of the fair trial issue will save all of the parties involved much additional litigation. The reason for this is that at this very time there is other litigation pending with other alleged infringers arising out of these very same patents. In the present posture of the case, in which the issue of estoppel will now become an issue of fact for the trial court in subsequent litigation arising out of the same patent, it certainly would be to the interests of all concerned that the issue be properly resolved now.

As this Court well knows, rebuttal testimony has especial importance in patent litigation. The reason for this is that the issue for the patentee is the issue of infringement. The issue of invalidity of the patent based upon either anticipation by prior art or obviousness as spelled out in 35 U.S.C. Sec. 102, 103, are affirmative defenses. It is not until the conclusion of the affirmative defense case in chief that the issue of invalidity is properly before the court. Thus, as far as the patentee is concerned, or his assignor, petitioner's evidence to sustain the validity of the patent is generally raised for the first time in rebuttal. Two important criteria for a fair trial were spelled out by this Court in *Blonder-Tongue Laboratories, Inc. v. University of Illinois Foundation*, *supra*, i.e., "whether without fault of his own the patentee was deprived of crucial evidence or witnesses in the first litigation." Regrettably, this very criteria is before the Court in this very case. Precisely, the petitioner contends that he was deprived of fair opportunity to produce rebuttal testimony to sustain the validity of the patent without his fault in that he offered the witnesses and the trial judge refused to consider their testimony. Further petitioner contends he was deprived of fair opportunity of cross-examination of respondent's principal witness, Steinman, whose very patent both the trial court and Sixth Circuit (erroneously) held to be pertinent prior art.

Specifically, the trial judge refused to permit cross-examination of Steinman on statements made in the file history of one of his patents about which Steinman testified on direct examination and which respondent offered as a prior art reference. It is incredible that a right of cross-examination on file history would be denied petitioner in such a situation particularly when the statements made in the file history are directly contrary to the findings and conclusions of the trial judge which formed the basis of affirmance by the Sixth Circuit under Rule 52(a) F.R.C.P. This point alone demands redress especially in view of the estoppel issue sure to come up in subsequent litigation. See *Alford v. United States*, 282 U.S. 687 (1931).

Equally prejudicial to petitioner was the denial of fair opportunity to offer rebuttal to the defense of invalidity raised in respondent's case in chief. The trial record is replete with attempts by petitioner to elicit testimony which would have successfully rebutted respondent's contention on invalidity through two experts, i.e., Yaeger and Stempel, both of whom were chemists highly skilled in the art involved.[7] This denial is directly contrary to concepts of

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[7] The following is a list of the various items of rebuttal evidence offered by plaintiff and excluded by the Court relating to the defense of invalidity, as well as answering on infringement:

(1) Yaeger's testimony as to the composition of insulating varnishes, contrary to Finding 90 (12:2420-22, 2437-40).

(2) Yaeger's testimony as to the meaning to him, as one skilled in the art, of Example 2 of Johannson Patent '304 DX-G, Tab 16 (7:1352-54), contrary to Finding 94.

(3) Yaeger's testimony as to the distinction, if any, between the compounds set forth in Col. 1 and continuing over to line 21 of Col. 2 of Patent '304, contrary to Findings 93, 94, 95, 96 (12:2419-20).

(4) Yaeger's testimony as to the relative effectiveness of allyl silanes v. vinyl silanes as coupling agents, contrary to Findings 52, 75, 79, 81 and Conclusions 15, 17, 18 (12:2413-17).

(Continued on following page)

the fair trial pronounced by this Court in *St. Paul Plow Works v. Starling*, 140 U.S. 184 (1891). To the same effect is *Maquire v. Federal Crop Insurance Corp.*, 181 F.2d 320 (1950); *Throckmorton v. Holt, et al.*, 180 U.S. 522 (1901); *National Surety Corp. v. Heinbokel, et al.*, 154 F.2d 266 (1946); *Zurich v. Wehr*, 163 F.2d 791 (1947); *Frankel v. Styer*, 386 F.2d 151 (1967).

While the record is replete with other instances in which petitioner simply was not given fair opportunity to present his case, we feel that these should be more aptly discussed in a brief on the merits rather than this petition. The fact still remains that this Court must be exceedingly vigilant to protect trial rights in a patent case in view of the drastic effect of a finding of invalidity in restricting patentee or his assignor from pursuing his rights against other infringers under the doctrine of estoppel.

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(5) Yaeger's testimony concerning his patent application disclosing vinyl silanes as coupling agents which was in Interference with Patent '378 and which would bear directly on the question of obviousness, specifically contrary to the Court's Finding 40 and Conclusion 11 (12:2417).

(6) Yaeger's testimony as to the sizes and coupling agents available in 1949 for treatment of textile fibers indicating a lack of obviousness almost five years after TeGrotenhuis' conception, specifically contrary to the Court's Finding 40 and Conclusion 11 on "obviousness" (12:2412-13).

(7) Stempel's testimony, as one skilled in the art, as to how the term "vinyl group" is used in Patent '378 and Patent '566, contrary to Finding 77 (12:2381-82).

(8) Stempel's testimony as to examples of compounds that differ by a CH_2 group that are not homologues, in rebuttal of testimony of Rochow (10:2074-75) and contrary to Conclusion 15 (12:2385-86).

(9) Stempel's testimony, as a chemist, as to the relative effectiveness of allyl silanes v. vinyl silanes as coupling agents, based on a reading of PX-158 (6:1043-48), a publication by defendant's employees Biefeld and Philipps, in rebuttal of testimony of Biefeld and Philipps on the publication (10:2101-03; 11:2259-60) and contrary to Finding 53 (12:2387).

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CONCLUSION.

This Court should render a clear delineation that the clear and convincing evidence rule applies to Rule 52(a) F.R.C.P. in patent cases to determine whether findings are clearly erroneous. The effect of this legal void has been a wide variety of differing opinions throughout the various circuits and within the Sixth Circuit itself when in fact uniformity in interpreting all the provisions of Title 35 is highly desirable. Furthermore, this Court has never clearly delineated the effect of Rule 52(a) F.R.C.P. to sustain an evidentiary finding of obviousness based upon non-reference prior art patents as part of the judicial construction of the patent laws of the United States. The result again in one context or another has been for varying results in the various circuits when uniformity is the desired objective. In particular, it is of great importance to patentees to understand whether when the patent exam-

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(10) Stempel's testimony as to the differences, if any, between a rubber and a resin, contrary to Finding 48 (12:2388).

(11) The Pyle Patent '391 (PX-157, 6:1040-42) giving an example of the making of a vinyl silane by the two-step Grignard process, old in the art in 1944 and described in the parent application (2:175), even for the limited purpose of impeachment (12:2422-23). It was previously offered for its substance contrary to Finding 65 (10:2088-90).

(12) Reports published by the U.S. Air Force of work at Bjorksten Research Laboratories (PX-70, 71 and 197; 5:716-66, 7:1217-91) representing work done by Yaeger, or under his direction and control, showing the superiority of vinyl silanes over allyl silanes as coupling agents contrary to Findings 52, 75, 79 and Conclusions 15, 17 and 18 (12:2427-28):

(13) Phillips and White Patent '569 (7:1297a) and part of the application on which it was based (7:1298-1300) containing an admission against interest by defendant that A-174 is a "vinyl silane," contrary to Finding 10 and Conclusion 9 (12:2431-34).

(14) PX-188 (6:1165-66), a publication of the American Chemical Society, substantiating Stempel's testimony there was no "chemical reaction" occurring in Example 2 of Johannson patent, contrary to Findings 85 and 94 (12:2377).

iner selects what to him, in his expertise, appears to be the most pertinent prior art reference, that the issuance of a patent against such a reference will be upheld at least as against a non-reference alleged prior art patent which contains the same language as the reference patent which has cleared the patent examiner who has issued the patent. Anything less not only will create chaos in the patent office and to patentees but will have a discouraging tendency to suppress (or stifle initiative) rather than develop invention.

For the foregoing reasons, it is respectfully contended that the within petition raises question of great public or general interest in the patent laws of the United States and the statutes pertaining thereto. Therefore, this petition should be granted.

Respectfully submitted,

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APPENDIX A.

OPINION OF THE COURT OF APPEALS.

No. 20845

UNITED STATES COURT OF APPEALS
FOR THE SIXTH CIRCUIT.

WESTWOOD CHEMICAL, INC.,
Plaintiff-Appellant,

vs.

OWENS-CORNING FIBERGLAS CORPORATION,
Defendant-Appellee.

APPEAL FROM THE UNITED STATES DISTRICT COURT
FOR THE NORTHERN DISTRICT OF OHIO.

Decided and Filed August 24, 1971.

Before: EDWARDS, CELEBREZZE and BROOKS, *Circuit Judges.*

BROOKS, *Circuit Judge.* This is an appeal by plaintiff-appellant, Westwood Chemical, Inc., owners of patents Nos. 2,742,378 and 2,481,566 (hereinafter '378 and '566) from a judgment of the District Court holding the patents invalid and finding that defendant-appellee, Owens-Corning Fiberglas Corporation, did not infringe the patents. *Westwood Chemical, Inc. v. Owens-Corning Fiberglas Corporation,* 317 F. Supp. 201 (N.D. Ohio, 1970). Patent '378 was granted on April 17, 1968, on application No. 302,415 filed August 2, 1952, and was a continuation-in-part of application No. 251,152 filed October 12, 1951, and of application No. 243,737 filed August 25, 1951, and of application No. 585,824 filed March 30, 1945. Patent '566 was granted on July 1, 1958, on application No. 302,415

filed August 2, 1952, and was a continuation-in-part of the same parent applications from which patent '378 originated. It was stipulated that in order for both patents to be valid it was necessary to receive the benefit of the earlier filing date of the parent application No. 585,824 filed March 30, 1945, on a continuation-in-part basis (35 U.S.C. § 120).

The substance of the invention claimed by its inventor, T. A. TeGrotenhuis, relates to treating fillers, pigments and fibers with unsaturated organo-silanes for use in reinforcing polyester resins and the resulting polyester resin bodies.[1] The invention claimed by patent '378 is the use of certain hydrolyzable silane chemicals having vinyl groups as coupling agents to reinforce the polyester resins. Patent '566 makes the claim of using hydrolyzable silane chemicals having alkenyl groups other than vinyl, specifically allyl silanes, as the coupling agent. Generally, the claimed objective of both inventions was to provide a resin, such as plastic or glass fibers, with greater strength and water resistance by treatment with the hydrolyzable silane chemicals.

As a preliminary matter, it is noted that the District Court in its conclusions of law numbered 6, 11, and 18-21, for various reasons, held both patents invalid. When this lawsuit was initiated plaintiff generally alleged infringement of the two patents. In response to a demand by defendant to specify which claims of the patents were allegedly infringed, plaintiff itemized claims 1, 2, 4, 6, 7, 8, 11, 14, 15-19, 21, 23-26 and 28 of patent '378 and claim 8 of patent '566. It was in this posture that the case went to trial. After trial plaintiff, in a post trial brief, attempted to remove from the Court's consideration all the allegedly

[1] Both patents are in the nature of process and product patents.

infringed claims of patent '378 except claims 11, 16 and 25, and the entire patent '566. Plaintiff now contends the District Court overstepped its authority in declaring both patents entirely void without defendant having sought declaratory relief. See *Sterling Aluminum Products, Inc. v. Bohn Aluminum & Brass Corporation*, 187 F. Supp. 879 (E. D. Mich. 1960), *aff'd.* 298 F.2d 538 (6th Cir. 1962). We agree. The District Court's holding of invalidity should only apply to the patents' claims directly in issue. *Bain v. M. A. Hanna Company*, 331 F.2d 974 (6th Cir. 1964), *cf. Goodwin v. Carloss Company*, 116 F.2d 644 (6th Cir. 1941). However, plaintiff further argues that the only claims in issue were those it itemized in its post trial brief. To this we cannot agree. Once the case went to trial and completion on certain specified claims, it was proper for the court to render a judgment as to those claims. Following a trial during which defendant has presented its case as to all claims in issue, plaintiff cannot without court permission, and in an ex parte fashion, be allowed to withdraw certain claims from the court's consideration. *Allegheny Steel & Brass Corporation v. Elting*, 141 F.2d 148, 149 (7th Cir. 1944); *Young v. McShain, Inc.*, 130 F.2d 31, 34 (4th Cir. 1942). Accordingly, while plaintiff could not withdraw from consideration by the court the claims in issue at trial, the court's holding must be limited to those specific claims and in so far as the judgment in this case may be construed to apply to those claims not placed in issue, it must be modified.

Because an affirmance of the District Court's holding of invalidity obviates the necessity to review the question of whether or not defendant infringed the patents,

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The District Court's decision on the question of infringement is found in its conclusions of law numbered 7-10, 317 F. Supp. 201 at 215-216. The Court held that defendant's practices did not infringe the patents.

we turn directly to the issue of invalidity. *Felburn v. New York Central Railroad Company*, 350 F.2d 416, 420 (6th Cir. 1965), *National Transformer Corporation v. France Manufacturing Company*, 215 F.2d 343 (6th Cir. 1954).

On the issue of the holding of the invalidity of the patents, the District Court made numerous findings of fact and conclusions of law which cumulatively negated practically every statutory requirement for validity of the patents in suit. Thus, the District Court found that the Court of Custom and Patent Appeals' decision in *TeGrotenhuis v. Yaeger*, 290 F.2d 951 (C.C.P.A. 1961) only resolved an interference issue as to whether TeGrotenhuis' 1945 application made sufficient disclosure of vinyl silanes and it did not, as plaintiff contends, reach or decide the question of whether or not the patent involved in the interference could validly receive the benefit of the earlier filing date of the 1945 application on a continuation-in-part basis. On this point, the District Court concluded that the patents could not receive the benefit of the earlier filing date because they were not properly based on valid continuation-in-part applications. Specifically, the Court held: 1. The 1945 application made no disclosure, implicitly or explicitly, as to glass fiber reinforced polyester resins and, therefore, the subsequent applications (upon which the two patents were based) covering glass fiber polyester resins could not receive the benefit of the 1945 filing date; 2. The 1945 application failed to teach a method for making hydrolyzable vinyl silanes and, therefore, the 1945 application cannot be used as a basis for these claims in the later applications; 3. The 1945 application did not disclose that vinyl silanes are superior coupling agents as compared with other known silanes and that this alleged superiority was the principal claim of patent '378; and 4. Allyl and vinyl silanes are equivalents (both are

included in the alkenyl silanes group) and the use of allyl silanes as coupling agents with polyester resins (the claim of patent '566) was disclosed in the pre-1945 art.

The District Court also concluded that TeGrotenhuis had all essential features of his invention taught him through a lecture on the subject by a Dr. Rochow and thus, there was a lack of required "invention." 35 U.S.C. § 102(f). Furthermore, the District Court found that the subject matter claimed by the TeGrotenhuis invention was known and used by others in this country before TeGrotenhuis invented it, 35 U.S.C. § 102(a), and the invention was made prior to TeGrotenhuis' effective date of conception, 35 U.S.C. § 102(g).[3] Lastly, the District Court concluded that the subject matter of TeGrotenhuis' invention was obvious at the time of invention to a person having ordinary skill in the art. 35 U.S.C. § 103.

The law is clear that a patent once issued is presumed valid, 35 U.S.C. § 282, and that a heavy burden of proof rests on the party attempting to prove invalidity. See *Ever-Wear, Inc. v. Wieboldt Stores, Inc.*, 427 F.2d 373 (7th Cir. 1970). However, a patent to be valid must meet all the requisite statutory requirements. See 35 U.S.C. § 101. And an invention which does not combine the three essential elements of novelty, utility and nonobviousness should not be given the privileged monopolistic status of a patent. *Monroe Auto Equipment Company v. Heckethorn Manufacturing & Supply Company*, 332 F.2d 406, 409-410 (6th Cir. 1964); *Zero Manufacturing Company v. Mississippi Milk Producers Association*, 358 F.2d 853,

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[3] Plaintiff argues his patents should be given priority because of alleged earlier date of conception and diligence to the time of reduction to practice, although subsequent to the others, 35 U.S.C. § 102(g), and that the District Court erred in not considering the diligence issue. However, because of our disposition of this case we do not reach this question.

855 (5th Cir. 1966). For the reasons hereafter stated, we affirm the judgment of the District Court as modified on the basis of its holding that the inventions claimed by the patents in issue were obvious to one having ordinary skill in the art. Thus, it is not necessary that we reach or decide the correctness of the District Court's alternative grounds for having held the patents in issue invalid.

This Circuit has approached the question of what constitutes "obviousness" through a three-step test prescribing what portions of the question turn on factual determinations and which are purely legal. The first step is "a determination of what the prior art was; this involves factual questions. Secondly, there is a determination of what, if any, improvement the patentee has made over the prior art; this will usually turn on expert testimony and therefore is a question of fact. The final step is to determine whether the improvement would have been obvious to one skilled in the art. This requires application of a legal criteria and therefore is a question of law, fully reviewable by the appellate court." *Monroe Auto Equipment Company v. Heckethorn Manufacturing & Supply Company*, *supra* at 411. The Supreme Court has also recognized the factual and legal composition of the question of obviousness. They have stated in *Graham v. John Deere Company*, 383 U.S. 1, 17 (1965), that:

> "While the ultimate question of patent validity is one of law, *A. & P. Tea Co. v. Supermarket Corp.*, *supra*, at 155, the § 103 condition, which is but one of three conditions, each of which must be satisfied, lends itself to several basic factual inquiries. Under § 103, the scope and content of the prior art are to be determined; differences between the prior art and the claims at issue are to be ascertained; and the level of ordinary skill in the pertinent art resolved. Against this background, the obviousness or nonobviousness of the subject matter is determined."

The District Court did an excellent job in determining the state of the prior art in a highly complex and technical area. There were the teachings of nine prior patents that were considered and plaintiff has challenged the inclusion of certain of these patents as prior art. There is possible merit to the challenge against the inclusion as prior art of the Steinman Patent No. 2,563,288. It is also arguable that the Witt Patent No. 2,649,396 is not proper prior art as against TeGrotenhuis patents, however, the other seven patents considered by the District Court are certainly prior art as against the patents in issue,[1] and the District Court's findings of fact as to the teachings of these patents are not clearly erroneous. Rule 52(a) Federal Rules of Civil Procedure, 28 U.S.C., *National Athletic Supply Corporation v. Tone-O-Matic Products, Inc.*, 421 F.2d 407, 408 (5th Cir. 1970); cf. *Payne Metal Enterprises, Ltd. v. McPhee*, 382 F.2d 541, 543 (9th Cir. 1967), which distinguishes conclusions of law from the clearly erroneous test.

Moreover, even if the District Court improperly considered these two patents as prior art, we cannot say that this amounts to reversible error when, as in this case, there is substantial competent evidence in the record which supports the District Court's conclusions of law. *Amerline Corporation v. Cosmo Plastics Company*, 407 F.2d 666, 669 (7th Cir. 1969); cf. *Kaiser Industries Corporation v. McLouth Steel Corporation*, 400 F.2d 36, 48 (6th Cir. 1968). Only a brief reiteration of the findings of the District Court as to the teachings of these prior patents is necessary here. The Court found:

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[1] In considering these other patents as prior art, we have accepted, for argument purposes only, that plaintiff in fact is entitled to the earlier filing date of its parent application. It must be observed, however, that the District Court found plaintiff was not so entitled, and our proceeding on the assumption that he was should in no way be construed as a definitive ruling on that question. See also n. 5 *infra*.

1. Johannson Patent No. 2,436,304 granted on application made June 11, 1943 taught and disclosed that treated glass fibers having allyl groups on the surface treated with methyl violet will react with the unsaturated allyl silane on the glass fibers. The object of the discovery was to "provide organophobic base members with adherent films which act as bonding agents for organic resins . . ." (and) "to provide a method for increasing adhesion on organic resins . . ." (and) "to provide an invisible and permanently attached priming coat on normally organophobic base members for the irreversible attachment of organic compositions." This Johannson Patent states that the invention was based upon the discovery that "organophobic surfaces become organophobic when treated with organo-silicon compounds comprising hydrolyzable organo-silicones, their hydrolysis products or their polymerized hydrolysis products, and that the adhesion or organic compositions such as resins, plastic . . . and the like to the organophobic surfaces thus provided is substantially greater than it is for the original untreated surfaces." The Johannson patent defines the suitable organosilanes for the process as "Alkenyl such as methallyl, allyl, etc." Example No. 2 of the patent claimed a process that treated glass fibers with a hydrolyzable allyl silane, methallylsilicon trichloride. Example No. 5 of the patent taught a positive chemical reaction occurs between a primer such as glass fiber surfaces, a coupling agent (an amino-organosilane) and a subsequent organic material (diazotized aniline hydrochloride). The TeGrotenhuis patent '566 claims the use of hydrolyzable silane chemicals having alkenyl groups other than vinyl, specifically allyl silanes, as coupling agents.

2. The Johannson Patent No. 2,557,787 was granted on a divisional application of the application upon which

Johannson Patent No. 2,436,304 was granted and, thus, has the benefit of the earlier filing date of June 11, 1943. 35 U.S.C. § 121. This Johannson Patent was directed to a method of "increasing the adhesion of organic resins to glass surfaces." The organo-silicon compounds used to treat siliceous surfaces so as to become organophilic were organo-silicon halides. The organo-silicon halides named included "alkenyl such as methallyl, allyl, etc." Expert testimony by a Dr. Rochow was to the effect that this Johannson patent taught the use of a vinyl type unsaturated substance as a coupling agent. And from this testimony the District Court found as a fact that the vinyl substance acting as a coupling agent was "a material which reacted with the absorbed water on the glass surface and established an organo-silane layer which later bond with the overlying material added on top of the coupling layer." The TeGrotenhuis patent '378 claimed the use of certain hydrolyzable silane chemicals having vinyl groups as coupling agents to reinforce polyester resins.

3. The Patnode Patent No. 2,306,222 granted on application made November 16, 1940, taught that glass surfaces, particularly fiber glass surfaces, become water repellant when treated with vapors of an organo silicon halide.

4. The Kropa Patent No. 2,465,731 granted on application made August 1, 1944, taught a method of preparing allyl chlorosilanes. The District Court also found that this patent made significant disclosures of the properties and uses of chlorosilanes.

These four patents were part of the prior art considered by the patent examiner in studying the applications for the TeGrotenhuis patents. The Johannson Patent No. 2,436,304 and Kropa Patent No. 2,465,731 were part of the prior art considered under TeGrotenhuis Pat-

ent No. 2,742,378. The Johannson Patents Nos. 2,436,304 and 2,557,786, Kropa Patent No. 2,465,731 and Patnode Patent No. 2,306,222 were part of the prior art considered under TeGrotenhuis Patent No. 2,841,566. Plaintiff correctly contends the fact that the patent examiner considered these patents when deciding on the question of the patentability of the claimed TeGrotenhuis inventions reinforces the presumption of validity which attaches to a patent once issued. *Scaramucci v. Dresser Industries, Inc.*, 427 F.2d 1309 (10th Cir. 1970); *Skil Corporation v. Cutler-Hammer, Inc.*, 412 F.2d 821 (7th Cir. 1969). But, on the other hand, the District Court also had properly before it three significant prior art patents as against the TeGrotenhuis patents which were not considered by the patent examiner. The failure of the Patent Office to consider pertinent prior art tends to weaken if not vitiate, the presumption of validity. *Reeves Brothers v. United States Laminating Corporation*, 417 F.2d 869 (2nd Cir. 1969); *B. F. Goodrich Company v. Rubber Latex Products, Inc.*, 400 F.2d 401 (6th Cir. 1968).

Of the three patents not considered by the patent examiner, the most revealing was Steinman Patent No. 2,513,268. This Steinman Patent (another Steinman Patent, No. 2,563,288, was considered by the District Court, but on the evidence it is questionable whether it was properly viewed as prior art) was granted on application filed December 30, 1944. The District Court found the patent taught a method of combining fibrous glass

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The District Court upon consideration of the evidence found that Dr. Steinman conceived his invention in 1943. We dismiss summarily plaintiff's claim that this was not a proper prior art patent because the court below failed to inquire into TeGrotenhuis' diligence from conception to reduction to practice. In so doing we reject the assumption of plaintiff's argument that the District Court erred in finding a conception date for this Steinman Patent earlier than TeGrotenhuis' conception date.

with resinous materials whose objective was providing "an adhesion-promoting agent, substances capable of polymerizing with the resin and reacting with the glass surface of the fibers to create a secure interbond between the dissimilar materials." Accomplishment of this objective was made by treating the glass fibers with allyl silicates. And the resultant improved properties from the treatment of the glass fibers were attributed "to the fact that unsaturated silicates are capable of copolymerizing with the resin to become in effect one with the resin surrounding the fiber surfaces. They also are believed to react by hydrolysis with the glass surfaces to be anchored securely to the fibers." From expert testimony, the District Court found that allyl silicates while not identical to allyl and vinyl silanes are functionally and structurally the same.

Another important prior art patent not examined by the Patent Office in issuing the TeGrotenhuis patents was Biefeld Patent No. 2,392,805 granted on application filed October 11, 1943. This patent taught that treatment of glass fibers with a composition including hydrolyzable organo-silane, e.g., "alkenyl such as methallyl, allyl, etc." (which were found to include vinyl silane), could be used to reinforce resins or plastics and the treated resin-glass fiber combination has tremendously added strength properties.

The last pertinent prior art patent scrutinized by the District Court was Hyde Patent No. 2,390,370 granted on application filed October 11, 1943. This patent was principally concerned with coating of "glass fibers particularly when grouped in strand or yarn form." The coating process was accomplished through the treating of glass fibers with hydrolyzable organo-silanes, including "alkenyl such as methallyl, allyl, etc." One of plaintiff's experts, a Dr. Price,

admitted that alkenyl also embraces vinyl. The Hyde Patent taught the usefulness of this treatment in promoting adhesion of certain varnishes to glass fibers. The importance of this patent, as well as the Biefeld Patent mentioned above, is in its disclosure that allyl and vinyl hydrolyzable silanes couple with glass fibers and that certain "desirable" properties result.

These factual determinations on the status of the prior art are not clearly erroneous and this Court is bound by them. The District Court concomitant with its consideration of the prior art heard testimony from expert witnesses on the subject of exactly what improvement the claimed TeGrotenhuis inventions made over the prior art. This is the second analytical step in determining obviousness as prescribed in *Monroe Auto Equipment Company v. Heckethorn Manufacturing & Supply Company*, 332 F.2d 406, 411 (6th Cir. 1964). As might be expected, there was conflict in the experts' testimony as to the significance of the improvement. Plaintiff's witnesses testified to remarkable and important advancement in the art as a result of the TeGrotenhuis contribution. Defendant's experts claimed TeGrotenhuis' inventions added nothing to the art. The Court found as a fact that the teachings of the TeGrotenhuis patents were either entirely or significantly portended by the prior art and little if any contribution was made to the existing art by the TeGrotenhuis inventions.

From these factual determinations—the state of the prior art and the improvement over the prior art made by the TeGrotenhuis inventions—the District Court resolved the legal question of whether the inventions in issue were obvious to one skilled in the art adversely to plaintiff. See *Conclusion of Law* No. 11, 317 F. Supp. 201 at 216 (N.D. Ohio, 1970). Our review confirms the legal correctness of

this conclusion. It seems apparent, given the state of the prior art and the improvement over the art made by TeGrotenhuis' inventions, that "there was an absence of that degree of skill and ingenuity which constitutes essential elements of every invention." *Hotchkiss v. Greenwood*, 52 U.S. (11 How. 248) (1851). The TeGrotenhuis inventions were of a nature that they were obvious to a person having ordinary skill in the art. 35 U.S.C. § 103.

Plaintiff argues that insufficient weight was given by the District Court to the important secondary indicia of nonobviousness such as commercial success, *Graham v. John Deere Company*, 383 U.S. 1, 17 (1965); *Application of Sponnoble*, 405 F.2d 578 (C.C.P.A. 1969); and long felt but unresolved need in the industry, *Young Corporation v. Jenkins*, 396 F.2d 893 (10th Cir. 1968). However, secondary indicia of nonobviousness are relevant and become supplementally useful only when there is a close question of whether the subject matter of an invention was obvious. *Kaiser Industries, Corporation v. McLouth Steel Corporation*, 400 F.2d 36 (6th Cir. 1968); *Waldon, Inc. v. Alexander Manufacturing Company*, 423 F.2d 91 (5th Cir. 1970). These secondary considerations, no matter how persuasive, cannot save the patentability of an invention when it clearly appears, as in this case, that the invention was obvious to one skilled in the art.

The last argument raised by plaintiff requiring comment is its allegation that it was denied a fair trial because of prejudicial rulings by the District Court on evidentiary matters. It is claimed that the District Court erred in not admitting certain crucial evidence, not excluding other evidence and in restricting plaintiff's cross-examination of one of defendant's witnesses. The record indicates that often the District Court ruled the way it did because it felt the evidence offered was repetitious, not

germane, or there was insufficient proof of expertise in certain textbook materials offered as authoritative documents. Respecting the allegations of improperly admitted evidence, it must be noted that in a trial to the court it is presumed that evidence which is improper will be disregarded by the court. *Processsteel, Inc. v. Mosley Machine Company*, 421 F.2d 1074, 1076 (6th Cir. 1970); *Taylor v. Taylor*, 211 F.2d 794 (8th Cir. 1954). Moreover, we have not been convinced that the admissions complained of were, in fact, erroneous.

On the issue of claimed error in the Court's ruling excluding certain evidence and restricting the scope of plaintiff's cross-examination, the burden of proving prejudice rests on plaintiff. *Voigt v. Chicago & Northwestern Railway Company*, 380 F.2d 1000 (8th Cir. 1967). Plaintiff has failed to prove that any of the evidence it wished to offer was more than cumulative, *Crown Cork & Seal Company v. Morton Pharmaceuticals, Inc.*, 417 F.2d 921 (6th Cir. 1969), or that the Court abused its discretion in limiting the scope of cross-examination. In short, plaintiff has failed to show that if any of the District Court's evidentiary rulings were erroneous, plaintiff's right to a fair trial was prejudiced. Rule 61, Federal Rules of Civil Procedure.

The judgment of the District Court is modified by restricting the determination of invalidity to the claims in issue, i.e., claims 1, 2, 4, 6, 7, 8, 11, 14, 15-19, 21, 23-26 and 28 of patent '378 and claim 8 of patent '566 and as so modified the judgment is affirmed.

APPENDIX B.

JUDGMENT OF THE COURT OF APPEALS.

No. 20,845.

UNITED STATES COURT OF APPEALS
FOR THE SIXTH CIRCUIT.

WESTWOOD CHEMICAL, INC.,
Plaintiff-Appellant,
vs.
OWENS-CORNING FIBERGLAS CORPORATION,
Defendant-Appellee.

JUDGMENT.

(Filed August 24, 1971.)

BEFORE: EDWARDS, CELEBREZZE and BROOKS, *Circuit Judges.*

APPEAL from the United States District Court for the Northern District of Ohio.

THIS CAUSE came on to be heard on the record from the United States District Court for the Northern District of Ohio and was argued by counsel.

ON CONSIDERATION WHEREOF, It is now here ordered and adjudged by this Court that the judgment of the said District Court in this cause be and the same is hereby modified by restricting the determination of invalidity to the claims in issue, i.e., claims 1, 2, 4, 6, 7, 8, 11, 14, 15-19, 21, 23-26 and 28 of patent '378 and claim 8 of patent '566 and as so modified the judgment is affirmed.

It is further ordered that the Defendant-Appellee recover from Plaintiff-Appellant the costs on appeal, as itemized below and that execution therefor issue out of said District Court.

Entered by order of the Court.

JAMES A. HIGGINS,
Clerk.

APPENDIX C.

ORDER OF COURT OF APPEALS DENYING REHEARING.

No. 20,845.

UNITED STATES COURT OF APPEALS
FOR THE SIXTH CIRCUIT.

WESTWOOD CHEMICAL, INC.,
Plaintiff-Appellant

v.

OWENS-CORNING FIBERGLAS CORPORATION,
Defendant-Appellee.

ORDER.

(Filed October 19, 1971.)

Before: EDWARDS, CELEBREZZE and BROOKS, *Circuit Judges.*

The petition of the petitioner for rehearing en banc has been considered. None of the judges of this Court who are in regular active service has favored ordering consideration en banc.

It is ORDERED that the petition is denied.

Entered by order of the Court

JAMES A. HIGGINS,
Clerk.

APPENDIX D.

FINDINGS OF FACT AND CONCLUSIONS OF LAW OF DISTRICT COURT.

No. C 63-460.

UNITED STATES DISTRICT COURT

NORTHERN DISTRICT OF OHIO,
EASTERN DIVISION.

WESTWOOD CHEMICAL, INC.,

Plaintiff,

v.

OWENS-CORNING FIBERGLAS CORPORATION,

Defendant.

July 29, 1970.

CONNELL, *District Judge.*

FINDINGS OF FACT.

1. The plaintiff in this case Westwood Chemical, Inc., is an Ohio Corporation, having its principal place of business at Olmsted Falls, Ohio. The business of the plaintiff was the sale of fatty acids, stabilizers for plastic materials and metal stearates for the rubber industry. The defendant, Owens-Corning Fiberglas Corporation is a Delaware Corporation, having its principal place of business at Toledo, Ohio. The business of the defendant corporation concerns the manufacture and sale of glass fiber and reinforced products.

2. This action, C 63-460, was filed June 10, 1963, against Owens-Corning Fiberglas Corporation and Johns-Manville Corporation. The original complaint contained

four causes of action. The first and second causes of action which charged violations of the Anti-Trust Laws of the United States, specifically 15 U.S.C. § 1 et seq. were dismissed, and the fourth cause of action containing allegations of infringement against Johns-Manville Corporation of the two patents in suit has been severed from this action. Therefore, only the third cause of action in the complaint stands, and it is this allegation upon which this suit was tried.

3. The third cause of action arises under the patent laws of the United States and alleges "infringement or actively inducing infringement and/or for contributory infringement of United States Letters Patent Nos. 2,742,378 and 2,841,566."

4. Also pending in this Court are actions against Ferro Corporation, Johns-Manville Fiber Glass, Inc., Union Carbide Corporation, Molded Fiber Glass Body Corporation, Certain-Teed Products Corporation and Dow Corning Corporation, Civil Actions Nos. C. 62-681, C 63-460, C 67-775, C 63-208, C 67-774, and C 67-787, respectively.

5. The defendant, Owens-Corning, has denied infringement and asserts affirmatively that each of the patents in suit is invalid on several grounds and is unenforceable by reason of fraud upon and misrepresentation to the Patent Office.

6. Jurisdiction is based on 28 U.S.C. § 1331 and § 1337.

7. U. S. Patent No. 2,742,378 (referred to as -378) was issued by the Patent Office April 17, 1956, and U. S. Patent 2,841,566 (referred to as -566) was issued by the Patent Office July 1, 1958.

8. The substance of this action relates to glass fibers treated with unsaturated organo-silanes for use in rein-

forcing polyester resins and the resulting polyester resin bodies.

9. Specifically, the alleged infringing practices of Owens-Corning are described in the document entitled "Commercial Textile Sizes and Mat Binders Employing Coupling Agents as Starting Materials" (PX-17) and a subsequent stipulation covered by a protective order (PX-18):

10. In the defendant's regular commercial operations it utilized four organo-silanes for treating glass fibers, the use of which is charged as an infringement. These organo-silanes are vinyl sodium silanolate (SS2D or SS2DN), vinyl trichlorosilane (A-150), vinyl trimethoxyethoxysilane (A-172) and methacryloxypropyltrimethoxysilane (A-174 or Z-6030). The first three are silanes and the fourth, A-174 or Z-6030 is neither a vinyl silane, allyl silane nor an alkylenyl silane (R. 962-68, 800-01, 1020; DX-Q, DX-KK).

11. The coupling compounds used by the defendant are applied to glass fibers from water solutions (R. 910-11).

12. Glass fibers treated with these coupling agents mentioned above are sold by Owens-Corning to purchasers who use the treated glass fibers for reinforcing polyester resins. Owens-Corning also uses some treated glass fibers for manufacturing tanks and the like, the glass fibers being used to reinforce polyester resins.

13. Owens-Corning first commercially sold glass fibers treated with vinyl sodium silanolate in early 1951 (R. 871). In 1951, Union Carbide commenced commercial production of vinyl trichlorosilane (A-150) and its use on glass fibers was commenced shortly thereafter by Owens-Corning (R. 1081-82). In late 1951 or 1952, Union Carbide commenced the manufacture of vinyl trimethoxy-

ethoxysilane (A-172) and its use was commenced shortly thereafter (R. 1082). The methacryloxypropyltrimethoxysilane (Z-6030 or A-174) was not developed until about 1962 (R. 963, 1082). Thereafter, the use of this coupling agent was commenced (R. 963-64).

14. In June, 1942, Dr. Steinman at Owens-Corning began the study of glass and more specifically its surface chemistry, its condition, and the chemicals which would react with glass; and with this knowledge in the field, the defendant corporation would then begin the development of a material that could utilize its good properties and minimize its weak tendencies.

15. Fiberglass-reinforced plastics or resins had been on the market since about 1940 (R. 501).

16. Glass fibers had been used commercially at this time and were found to be a successful material for the reinforcement of resinous material such as phenolic resins. Glass fibers were being used prior to the advent of unsaturated polyester resins; the next logical step was the attempted combination of glass fibers with this new polyester resin. The purpose of the combination of these two materials would be the added strength the glass fiber, an inorganic material, would give to the polyester resin.

17. Unsaturated polyester resins were developed during World War II (PX-23, p. 13; PX-24, p. 8; PX-25, p. 14; PX-22, p. 19). Due to the War, the resins were unavailable to private concerns and were restricted to governmental use until mid-1945 (PX-23, p. 14).

18. It was found at this time that there was a fair amount of water held on a glass fiber surface by bonds called hydrogen bonds (R. 1143-44). More specifically, the glass surface is composed of as many as 50 to 300

layers of water held to the glass fiber surface through hydrogen bonds.

19. It was found that chlorosilane would react with the hydroxyls on the glass surface permitting lubricity. This brought about the beginning of the "double fish-hook" theory (R. 1145). This theory purposes that the coupling agent at one end reacts with the glass fiber surface, and the other end reacts with the resinous material by copolymerization (DX-G, Tab 24, Col. 4, 11.28-35; R. 1141-45).

20. In May 1940, Dr. Rochow discovered that methyl chloride could be brought to reaction with elementary silicon to produce methyl chlorosilanes (R. 624). Soon after this discovery, Dr. Rochow's colleague, Winton Patnode, was able to produce methyl chlorosilane in larger quantities.

21. Furthermore, Winton Patnode showed Dr. Rochow that the reaction of vapors of methyl chlorosilane with glass made it water repellent due to the fact that the methyl chlorosilane had reacted with the water surface on the glass. The result was a thin film or layer of methyl-siloxane on that glass surface (R. 627).

22. Dr. Steinman and others at Owens-Corning began the use of organic-silicon compounds in treating glass fibers for the purpose of obtaining lubricity; more specifically the application of dodecyl trichlorosilane to glass fibers.

23. In the middle of February 1943, Dr. Steinman disclosed to Mr. Philipps and later about March 1943 he made the same disclosure to Mr. Overman of his concept of using allyl silanes and silicates as a coupling agent to bond glass fibers to laminating resins (R. 1142, 1101).

24. In June, 1943, Dr. Steinman discussed with Dr. Andregg the double-fishhook theory that Owens-Corning had for improving glass fibers. This discussion included the application of unsaturated silanes to glass fibers.

25. Dr. Steinman made an allyl silane in 1943. The preparation of these allyl silanes being difficult and dangerous; Dr. Steinman was requested by Owens-Corning to end all preparation of these products and made arrangements with Dow Corning to supply him with any silane he needed (R. 1164-65, 1101).

26. Dow Corning was unable to supply allyl silanes immediately, and after repeated requests, Dow Corning was finally able to furnish Owens-Corning with the allyl silanes in mid-1945 (R. 1171, 1101-02).

27. Because no allyl silanes were available from Dow Corning, Dr. Steinman concentrated his efforts in the area of allyl silicate materials; as a result, the silicates were made and evaluated.

28. In testing these, it was found that the allyl silicate was the first material to show improved physical properties by thirty to forty percent in compression, flexure and tensile strength (R. 1166-67).

29. The allyl silicates are structurally very similar to the allyl silanes, the only difference being that in the silane the allyl group is attached directly to silicon, whereas in the silicate the allyl group is attached to silicon through oxygen. The coupling mechanism by which each of these function in a glass fiber reinforced polyester resin is the same.

30. The unsaturation of the allyl group in each provides one fishhook which copolymerizes with the unsaturated polyester resin. The silicon and hydrolyzable group on the other end of the molecule acts as the other

fishhook, whereby the silicate or silane is bonded to the glass surface through the hydroxyl groups on the surface of the glass fiber (R. 1167-68, 1107-08).

31. In comparison, the allyl silicate did not bond as well as the silane due to the fact that the strengths of the laminates made with the silanes were far better than that of the silicates (R. 1108).

32. This strong performance of the silicate gave added impetus in obtaining allyl silanes (DX-Z; DX-AAA; R. 1167-68).

33. In late July, 1945, Dow Corning was finally able to supply the first unsaturated silane (R. 1180, 1102).

34. The testing of these silanes took place immediately with the expected, good results (R. 1103; DX-BBB, pp. 90 et seq.; R. 1177-87; DX-DDD; DX-GGG).

35. The end result was the sale of glass fibers treated with an allyl silane, specifically diallyl diethoxy silane (OPT. 2), to the Shakespeare Company for use in their fiberglass reinforced polyester resin fishing rods (R. 1211, 1104, 870).

36. The diallyl diethoxy silane was used commercially in Finish 113 until the early 1950's (R. 870). About the same time, duPont developed an organic chrome complex sometimes called a Werner or Volan complex (R. 1079); the purpose being for incorporation in glass to improve adhesion of glass fibers to resins. The organic portion of this finish was a methacrylate which contained unsaturation and would copolymerize with the unsaturated polyester resins (R. 1107-08). This process was incorporated in Finish 114 and used in 1946, and was still in service in 1964 (R. 310; PX-107, p. 41).

37. In 1949, Union Carbide was making and sampling vinyl silanes in a pilot plant (R. 1081).

38. Vinyl silane first became commercially available in small quantities in late 1950 and early 1951, and the use has increased ever since (R. 893, 1081).

39. In late 1949, the United States Air Force contracted with Bjorksten Research Laboratory to develop a means of improving the adhesion of glass fibers to polyester resins (PX-194). Bjorksten Laboratory surveyed the industry and after about six months of testing and evaluation, Mr. Yaeger noted a bottle of vinyltrichlorosilane, furnished Bjorksten by Union Carbide, and thought it would make a good coupling agent (R. 1331). This experiment was tried and found to be effective (R. 1332). Bjorksten's result was a sizing compound of vinyl trichlorosilane and beta-chloroallyl alcohol. This finish was not a straight vinyl silane type of finish and had in it both the vinyl silane and an allyl derivative. This finish was applied from a solvent system and never became commercially used because of the hazards of volatility and the expense involved in using solvent systems. (R. 909-10, 337; PX-72).

40. Due to the discovery of methods of preparing the vinyl silanes, Owens-Corning utilized the vinyl silanes in the double fishhook concept of Dr. Steinman since the function of the allyl silane and the vinyl silane are identical (R. 1105-07).

41. In early 1951, Owens-Corning utilized a finish called Finish 136, which includes a vinyl silane as a coupling agent called vinyl sodium siloxanolate known commercially as SS2D or SS2DN (R. 870-71).

42. Owens-Corning now sells and has sold glass fibers treated with SS2D since 1951 (R. 871). Its use of sodium siloxanolate is charged as infringement in this suit.

43. In 1951, Union Carbide had developed vinyl trichlorosilane, designated A-150, to the point of making it available as a useful commercial material. Shortly thereafter, additional finishes based on this product were quickly developed (R. 1081-82).

44. The Garan finish, or coupling agent, invented by Dr. Steinman became available for use in 1951 (R. 1136-37). And in late 1951, a vinyl, trimethoxyethoxysilane which is designated A-172 was produced (R. 1082). All these finishes are still in use today (PX-107, p. 41).

45. In early 1962, Union Carbide introduced the compound known as A-174 and also known as Z-6030 by Dow-Corning. This compound is sold today and is an organic silane in which the organic portion is a methacrylato group (R. 963, 1082). The use of these materials is also charged as an infringement.

46. Mr. T. A. TeGrotenhuis was a patent attorney and chemical consultant for the General Tire and Rubber Company (R. 417). During the period from late 1941 until November 1944 he was consulting for General Tire and performing duties with respect to the preparation of a synthetic latex that could be used in place of natural latex. Mr. TeGrotenhuis was also working on the problems of improving the reinforcement of high polymers such as rubber with various inorganic solids.

47. On November 15, 1944, Mr. TeGrotenhuis attended a lecture given to the Cleveland Engineering Society by Dr. Rochow of General Electric. During the lecture Dr. Rochow demonstrated the properties of the organo-silane compounds, pointing out that organochlorosilanes would hydrolyze and, therefore, when brought into contact with a glass surface, they would react with the

water adsorbed on that flass surface, and deposit a highly water repellent film of an organic siloxane attached to the glass, just as the adsorbed water had been (R. 636-37; PX-4). The second aspect of Dr. Steinman's double fish-hook concept, being that the unsaturated groups of the organo-silanes would react and copolymerize with polyester resins, was well known at this time to those working in the art.

48. Mr. TeGrotenhuis wrote a memorandum (PX-4) proposing to treat pigments for rubber, paint, printing ink and the like with silanes. However, his memorandum made no reference to the treatment of glass, it did not state the portion of the organic silane to be used, nor did it refer to polyester resins or to glass fiber reinforced polyester resins.

49. Mr. TeGrotenhuis performed only five of the seventeen examples stated in his original application of March 1945. No experiments were made with glass, glass fibers, polyester resins or unsaturated silanes (R. 499). Mr. TeGrotenhuis does not claim to be the inventor of fiberglass reinforced resins or plastics, nor does he claim to be the inventor of any of the polyester resins disclosed in the patents in suit. The plaintiff does not claim to have invented glass fiber reinforced resins having a bond between the fibers of the resins, nor does he claim to have invented the use of organo-silicon compounds on glass surfaces to provide a coating integral with the glass surface, nor did Mr. TeGrotenhuis discover that allyl silanes would adhere tenaciously to glass, nor did the plaintiff discover that unsaturated silanes would copolymerize with unsaturated polyester (alkyd) resins, nor did the plaintiff discover that alkenyl organo-silanes, which includes allyl organo-silanes and vinyl organo-silanes, are useful for coating glass fibers, nor did the plaintiff discover that

organo-silicon compounds are capable of copolymerizing with monomers (R. 516-18; 422-25; 553-54; 564-65).

50. Mr. TeGrotenhuis claims to have contributed "Those broadly having an alkenyl group carried by silicon in combination with interpolymerized resin" (R. 518).

51. Mr. TeGrotenhuis claims to be "the inventor of glass surfaces or solid inorganic surfaces which have vinyl groups attached integrally with the surface of the glass or such solid" (R. 518).

52. The -378 and -566 patents assert that vinyl silanes are superior in performance to the allyl silanes (R. 577). This alleged fact has been contradicted by plaintiff's witness (R. 248) and to the truth of this contradiction the defendant's experts concur (R. 1105, 1085, 780-81, 872-77).

53. Mr. TeGrotenhuis has made no tests with respect to the reactivity of the two silanes. The record shows that he relied on what he had "seen in the literature for the different results where the vinyl gives a much higher, much superior result." (R. 580, 590).

54. The patent application of Mr. TeGrotenhuis filed in March, 1945, did not mention glass fibers or glass fiber reinforced polyester resins (R. 502). The 1945 application mentioned only rayon, nylon and cotton (R. 503). Mr. TeGrotenhuis in his 1945 patent failed to mention or even allude to glass, or glass fiber reinforced polyester resins. The failure to mention glass while mentioning the others fibers was "because it was so obvious" (R. 502). The specific fibers mentioned were organic fibers, which refers to the chemistry of the hydro-carbons and their derivatives, while on the other hands, glass is an inorganic fiber and falls in a different chemical category referring to those chemical compounds not containing carbon (PX-3, p. 1720; R. 503-04). The first mention of glass fiber or

glass fiber reinforced polyester resins in a United States patent application filed by Mr. TeGrotenhuis was in an application filed in 1951 (PX-7).

55. The TeGrotenhuis patent No. 2,742,378 (PX-1) issued on April 17, 1956 on application Serial No. 302,415 (PX-9), filed August 2, 1952, is alleged to be a continuation in part of application Serial No. 243,737, filed August 25, 1951, and of application Serial No. 585,824 filed March 30, 1945 (PX-7 and PX-5, respectively).

56. Patent No. 2,841,566 (PX-2) issued on application Serial No. 439,463 (PX-10) was filed June 25, 1954. That application purports to be a division of application Serial No. 302,415 filed August 2, 1952, which was a continuation-in-part of application Serial No. 585,824, filed March 30, 1945.

57. As to the -378 patent, plaintiff relies on claims 1, 3, 4, 6, 7, 8, 11, 14, 15-19, 21, 23-26 and 28 and has specified claims 11, 16 and 25 as example claims. As to the -566 patent, plaintiff relies on claim 8.

58. The plaintiff has stated that "we will be willing to stipulate that we must carry our date back to the date of the March 30, 1945 application" (R. 13). Therefore the validity of the -566 patent and the -378 patent as a matter of law and by stipulation of the parties must have the benefit of the March 30, 1945 application, Serial No. 585,824 in view of the existing prior art.

59. Both patents, -378 and -566, pertain to the treatment of fillers, pigments and fibers with an organo-silicon compound, referred to as a coupling agent, which forms a bond with the filler, pigment or fiber and with a polyester resin into which the reinforcing material is placed. The claims of -378 patent are addressed to the use of a vinyl silane as a coupling agent; whereas, the single claim

of the -566 patent in issue, namely claim 8, is broadly addressed to a coupling agent having an alkylenyl (alkenyl) group other than vinyl.

60. The TeGrotenhuis application Serial No. 585,824, filed March 30, 1945 admittedly resulted from the teachings of Dr. Rochow that organo silicon compounds could be bonded to glass surfaces, and that those organo silicon compounds, if unsaturated, would copolymerize with monomers such as styrene (R. 636-37, 565). Again this Court points out that the March 1945 patent makes no reference to glass or glass fibers (R. 502-04).

61. The 1945 application was entitled "Pigmented Compositions and Methods of Making Same." The scope of the invention encompasses pigmented compositions and methods of making pigmented compositions; and it made no reference to glass, glass fibers or the treatment of glass or glass fibers with organo-silanes (PX-5, p. 1). The list of compounds in the application includes practically all conceivable hydrolyzable organo-silicon compounds, which literally encompasses millions of compounds (R. 896). There is also disclosed organo-silicates as well as organo-silanes. This list also includes both allyl and vinyl silanes among the millions of compounds disclosed; however, no distinction is made between them. No statement is made in this patent as to the superiority of vinyl silanes as opposed to allyl silanes or any other unsaturated silanes (R. 894).

62. After general disclosures, the original application set forth some specific examples. One group relates to the preparation of treated pigments, specifically carbon black and titanium dioxide (PX-5, pp. 8-9). Another group related to the preparation of a type of rubber compounds in which the treated pigments were incorporated (PX-5,

pp. 10-14). The third group is directed to the preparation of printing inks and coating compositions in which the treated pigments were incorporated (PX-5, pp. 15-17). The fourth group was directed to the preparation of synthetic fibrous material, specifically rayon, in which the treated pigments, carbon black and titania were incorporated to color the fiber (PX-5, p. 8). Finally, one example was given for the preparation of finely divided pigments, specifically cement clinkers (PX-5, pp. 19-21).

63. This 1945 TeGrotenhuis application, of which the plaintiff must have the benefit, makes reference to hydrolyzable vinyl silane. Plaintiff's witness, Dr. Price, stated that there was "no disclosure in the art as of March, 1945 of making vinylhydrolyzablesilane" (R. 239). This statement of fact was further verified when Dr. Rochow admitted that there was not available or procurable any vinyltrichlorosilane or any other vinyl hydrolyzable silane until the work of Dallas Hurd in the fall of 1945 (R. 621).

64. The 1945 application of T. A. TeGrotenhuis suggests several methods for making organo-silicon halides. The first method was the use of a Friedel-Crafts catalyst (PX-4, p. 6, l. 15). Dr. Kanner attempted to make a hydrolyzable vinyl silane by this method and could not do so (R. 958-59; DX-HH; DX-II). Dr. Henry Gilman, also speaking authoritatively on this subject, stated positively that in 1945 a hydrolyzable vinyl silane could not be made by this method (R. 1011-13).

65. In this 1945 patent, T. A. TeGrotenhuis suggested the possibility of making these silanes by a Grignard synthesis (PX-5, p. 6, l.16). Dr. Gilman stated with respect to the amount of times he used the Grignard synthesis, "it is conservative to state that it is in the thousands." And on two occasions prior to 1945, he tried to prepare a vinyl Grignard reagent in connection with his

own work, and failed in both instances. It was not until after 1945 that the first vinyl Grignard reagent was successfully made (R. 1009-11).

66. Mr. Te Grotenhuis suggests in his 1945 application the preparation of silanes by a Wurtz synthesis (PX-5, p. 6, l. 16). To this statement, Dr. Gilman testified that vinyl hydrolyzable silanes were not recoverable from the Wurtz synthesis (R. 1016) as set forth in the 1945 application.

67. The 1945 TeGrotenhuis application listed seven patents as teaching the preparation of organo-silicon halides (PX-5, p. 6, 11, 2-30). Upon examination of these patents, Dr. Kanner testified that there is no disclosure in any of these patents of any method of preparing a vinyl hydrolyzable silane (R. 968-69).

68. The 1945 TeGrotenhuis patent suggests the possibility of preparing a vinyl silane (butadienyl silicon halide) by a Grignard synthesis from silicon tetrachloride and chloroprene. Dr. Van Auken of Union Carbide attempted to carry out this reaction and using the best methods known failed in these experiments and "we tried all of these things several times." His conclusion was that it could not be done (R. 935-37; DX-DD). Independent of Dr. Kanner's experiment, Dr. Aufdermarch of duPont attempted the same reaction and failed (R. 900-04; DX-CC). In attempting to prepare Grignard reagents from chloroprene, "we tried to carry out this reaction and we couldn't get it to do so * * *. We tried all the various tricks that chemists know to get the reaction to initiate * * * and it was to no avail because we couldn't get the reaction to go" (R. 901).

69. The TeGrotenhuis application, Serial No. 243,737, was filed August 25, 1951 after the defendant began the commercial use of both allyl silanes and vinyl silanes on

glass fibers for use in reinforcing polyester resins (R. 870, 871).

70. This application stated that it was "a division or continuation-in-part of my application Serial No. 585,824 filed March 30, 1945 * * *" (PX-7, p. 1). This application contained new subject matter not included in the 1945 application. Due to this new disclosure the Patent Office referring specifically to Example 1, relating to dry glass fabric requested cancellation as to this reference (PX-7, p. 17).

71. The 1951 application, Serial No. 243,737, filed August 25, 1951, was limited to unsaturated organo-silicon compounds and included both the silanes and the silicates. Whereas the 1945 application included practically all conceivable organo-silicon compounds, the saturated and unsaturated silanes, the silicates, and the aromatic silanes, etc. (PX-7, p. 2).

72. In this patent, both the allyl silanes and the vinyl silanes are disclosed and treated as equivalents for their intended purposes. There is no preference suggested for the vinyl silanes in this application.

73. It is to be pointed out that in the 1951 application, Mr. TeGrotenhuis made an oath that no application had been filed "on this invention or discovery," in any foreign country. It is noted by this Court that patent applications had been filed in Australia, France and Great Britain in 1947 which closely correspond to the 1945 application (PX-80, 82). However, the required oath accompanying the 1951 application as well as the oaths accompanying the -378 and -566 patents claim that this is the first of this particular discovery.

74. The Patent Office recognized that the 1951 application contained new matter not included in the 1945

application and required a cancellation of the statement that the 1951 application was a "division" of the 1945 application (PX-71, pp. 1, 17). The Examiner specifically referred to the disclosure of dry glass fabric as constituting new matter not contained in the original 1945 application (PX-7, p. 17).

75. The Examiner also held that the claims directed to vinyl silanes were obvious in view of the teachings of the prior art regarding the use of allyl silanes. "Nothing patentable is seen in substituting the claimed vinyl silicon compounds for allyl silicon compounds in this reference, especially since there is no indication that any unusual or unexpected results are obtained thereby" (PX-7, p. 17). At this time, Mr. TeGrotenhuis then asserted that vinyl silanes are superior to allyl silanes (PX-7, p. 28). According to the testimony given by both plaintiff's and defendant's witnesses, the two silanes are equivalent (R. 248, 236-37, 787, 872-77, 1083-87, 1106-08).

76. At this point, the Patent Office referred to Mr. TeGrotenhuis's interference attempt against the Steinman patent, and specifically held that the 1945 application did not disclose glass fibers (PX-7, pp. 39, 46).

77. Also this Court points out that Mr. TeGrotenhuis represented that "vinyl" and "vinyl group" by definition require the double bonded carbon to be attached to silicon (PX-7, p. 132). This statement is correct; however, in A-174 and Z-6030, the double bonded carbon is separated from the silicon atom by at least four carbon atoms and one oxygen atom (R. 800-01, 962-68; DX-Q).

78. The TeGrotenhuis application Serial No. 302,415, filed August 2, 1952, eventually issued as the -378 patent; one of the two patents in suit (PX-9). This application was directed to the treatment of pigments and fibers; whereas, the 1951 application was directed to fibers only.

79. This application again contained the scientifically incorrect statement that vinyl silanes are superior to other silanes (PX-9, pp. 32-47). This statement made by Dr. Urbanic (PX-9, p. 101) is not supported by any tests or any recognized authority, or by any of the witnesses.

80. The oath accompanying the 1952 application made no reference to the 1945 application. The assertion that the -378 patent was a "division or continuation-in-part" of the March, 1945 application (PX-9, p. 1) was ordered stricken by the Examiner; pointing out that Examples 1 to 4 which related to glass fabric constituted new matter (PX-9, p. 24).

81. This application, stating the preference of vinyl silanes over other silanes, is based on an incorrect statement which has already been discussed. It is noted by this Court that this application was filed one day after the amendment in the 1951 application, Serial No. 243,737, in which Mr. TeGrotenhuis first incorrectly asserted the superiority of vinyl silanes. It is further noted that there were prior art references cited and that the only new discovery was the alleged superiority of vinyl silanes. It is noted that the oath accompanying this application was not the proper oath for a continuing application. (See 37 C.F.R. § 318, and compare with PX-9) and it made no reference to the 1945 application.

82. The application Serial No. 439,463, which was filed June 25, 1954 as a division of application Serial No. 302,415, eventuated into the -566 patent in suit (PX-10). This patent is also claimed to be a continuation-in-part of the 1951 application Serial No. 243,737 and the 1945 application Serial No. 585,824 previously considered (PX-10, p. 1).

83. The specification, as filed, was very similar to the original specification of application Serial No. 302,415,

But, as in application Serial No. 302,415 and application Serial No. 243,737, the specification was significantly different from the specification of application Serial No. 585,824 (PX-9, p. 1; PX-7, p. 1; PX-5, p. 1). The principal difference between the Serial No. 439,463 specification and the Serial No. 302,415, specification was that the broad references to the unsaturated or olefinic silanes were replaced by references to allyl silanes; and the references to vinyl silanes were deleted (See and compare, PX-9, p. 3 to PX-10, p. 3).

84. The oath in this application referred to the original 1945 application, however, the requisite averments regarding the subject-matter not common with tne 1945 application were not made. No averment was made regarding the foreign applications or foreign patents on the subject matter not common to the 1945 application. The 1947 French application had been filed in France disclosing and had claimed subject matter not common to the 1945 application, namely, glass fibers and glass fabric. A French patent had issued June 18, 1952 (PX-80A, p. 17) on this application prior to the filing date of application Serial No. 439,463.

85. It is noted by this Court that with respect to the prosecution of the -566 patent, Mr. TeGrotenhuis in making reference to the Johannson Patent No. 2,436,304 (DX-G, Tab 16), asserted that there was no disclosure "of any material having allyl groups on the surface * * * reacted with another monomer" (PX-10, p. 26). It is noted that Example 2 of that patent taught that treated glass fibers having allyl groups on the surface treated with methyl violet, an olefinic unsaturated compound having conjugated double bonds, will react with the unsaturated allyl silane on the glass fibers (R. 678-87). The plaintiff states that polystyrene could not have any residual unsat-

uration to react with the allyl groups. However, the testimony of Dr. Rochow shows that there is sufficient monomer remaining in polystyrene to react with all the allyl groups present on the treated fibers (R. 760-66; DX-O).

86. The Patnode Patent No. 2,306,222 (DX-G, Tab 3), which issued on an application filed on November 16, 1940 teaches the use of organo-silicon halides on glass products. This patent teaches that glass surfaces, and specifically the surface of glass fibers, when treated with vapors of an organo-silicon halide become water-repellent (R. 644-45). Patnode teaches that the treatment provides the glass surface with an invisible, tightly adherent water-repelling surface, which becomes integral with the glass (DX-G, Tab 3, P. 1, Col. 2, ll. 3-13). Patnode explained the mechanism by which the film attached, stating that "organo-silicon halide vapors react with an adsorbed film of water to form the corresponding silicol, which is strongly adsorbed" (DX-G, Tab 3, P. 2, Col. 1, ll. 45-50; R. 645).

87. In the lecture that Dr. Rochow gave to the Cleveland Engineering Society on November 15, 1944, the substance of the Patnode patent was presented and demonstrated (R. 644-30).

88. The Hyde Patent No. 2,390,370 (DX-G, Tab 7) issued on an application filed October 11, 1943 is directed "to coatings for glass fibers particularly when grouped in strand or yarn form" (Page 1, Col. 1, ll. 1-3); and teaches the treating of glass fibers with hydrolyzable organo-silanes to protect the surfaces of the fibers and hold the fibers together as a strand (R. 646).

89. The hydrolyzable organo-silanes taught as suitable include "alkenyl such as methallyl, allyl, etc." (P. 2, Col.

1, ll. 60-61). Plaintiff's expert, Dr. Price, points out that "alkenyl" embraces vinyl, and that vinyl is the simplest alkenyl (R. 183). Dr. Rochow and Dr. Jellinek agree that the "etc." taught that vinyl silane was within the scope of the patent (R. 661, 1087). Here it can be clearly seen that Hyde teaches the use of both allyl and vinyl hydrolyzable silanes on glass fibers.

90. The Hyde patent further teaches that the organosilane coating is useful in promoting the adhesion of electrical insulating varnishes to glass fibers (DX-G, Tab 7, P. 4, Col. 1, ll. 10-22). The insulating varnishes contain unsaturated groupings and harden by a process of air-induced polymerization (R. 647, 652). Such varnishes contain liquid polymerizable monomers (R. 650), and when an alkenyl silane is placed on glass fibers, as taught by Hyde, and an insulating varnish is applied to the treated fibers, the result is the "hardening or polymerization of the insulating varnish fastening itself to the underlying alkenyl siloxane and polymerizing in place" (R. 652).

91. The Biefeld Patent No. 2,392,805 (DX-G, Tab 8) issued on an application filed on October 11, 1943 is directed to the manufacture and protection of glass fiber strands (R. 659). It teaches the treatment of glass fibers with a composition which includes a hydrolyzable organosilane; and it teaches that suitable hydrolyzable organosilanes include "alkenyl such as methallyl, allyl etc." which icludes the vinyl silanes, substituted vinyl silanes, butenyl silanes and allyl silanes (R. 659-61). One purpose in so treating the glass fibers is (Page 1, Col. 2, ll. 40-49):

> "to provide a heat-resistant lubricant and binder that are compatible with a large number of resins. This aspect of the invention is important where the yarns, strands or fabrics are used to reinforce plastics or to

be combined with resins in the manufacture of electrical insulation and plastic laminates. In many cases lubricant and binder of the invention may act to actually increase the adhesions of the plastics or resins to the surfaces of the fibers."

Biefeld also states (P. 3, Col. 1, ll. 71-Col. 2, l.3):

"An added advantage of the present invention is that the coating materials are compatible with a large number of resins and, since they also adhere strongly to the fiber surfaces and are not adversely affected by the heat used to cure the resin, the strength of resin-glass fiber combinations such as plastic laminates is markedly bettered."

92. It can be seen by this patent, that Biefeld specifically teaches the treating of glass fibers with allyl and vinyl silanes and using the treated glass fiber for reinforcing resins or plastics. Furthermore, it teaches that such a treatment will improve the adhesion of the reinforcing fiberglass to the resin (R. 661-62).

93. The Johannson Patent No. 2,436,304 (DX-G, Tab 16) was issued on an application filed June 11, 1943 and is directed to "coatings on solid or fibrous bodies" (Col. 1, ll. 1-3). It teaches that (Col. 11, ll. 30-44; See also Dr. Rochow, (R. 678-79):

"Another object is to provide organophobic base members with adherent films which act as bonding agents for organic resins, lacquers and the like.

Another object is to bond organic resins, lacquers and the like to base members of siliceous character.

Another object is to provide a method for increasing the adhesion on organic resins, lacquers and the like to glass surfaces.

Still another object is to provide an invisible and permanently attached priming coat on normally organophobic base members for the irreversible attachment of organic compositions."

The patentee Johannson states that the basis for his invention is (Col. 1, ll. 44-52):

> "My invention is predicated upon my discovery that organophobic surfaces become organophilic when treated with organo-silicon compounds comprising hydrolyzable organo-silicanes, their hydrolysis products or their polymerized hydrolysis products, and that the adhesion or organic compositions such as resins, plastics, lacquers, paints, dyes and the like to the organophilic surfaces thus provided is substantially greater than it is for the original untreated surfaces."

The patentee, Johannson, defines the organo-silanes which are suitable and specifies among others, "alkenyl such as methallyl, allyl, etc." (Col. 2, l. 18; R. 689). Johannson then describes the practice of the invention as follows (Col. 2, l. 49, to Col. 3, 1, 2):

> "In the practice of my invention a primary coating is applied to the base member by contacting the latter with one or more of the aforesaid hydrolyzable organo-silicanes, their hydrolysis products as priming agents and thereafter another organic material such as a resin, plastic, gum, lacquer, paint, dye or the like, is applied to the treated surface of the base member."

94. The examples given by Johannson include all the essential elements of the claims of the patents in suit. In Example No. 2 (Col. 2, ll. 65-75), glass fibers were treated with a hyrolyzable allyl silane, namely, methallylsilicon trichloride. Thereafter the treated fibers were brought into contact with methyl violet dye, which contains conjugated double bonds (R. 681; DX-L). The allyl silane (methallylsilicon trichloride) also contains double bonds as does the methyl violet (R. 686-87). Therefore, when the treated glass fibers of Example No. 2 are brought into contact with methyl violet, a reaction takes place between

the double bonds of the treating agent (the methallyl groups on the glass) and the conjugated double bonds of the methyl violet (R. 687).

95. Example No. 5 of this patent (Col. 4, ll. 25-38) also teaches a positive chemical reaction between a primer (glass fiber surface), a coupling agent (an amino organo silane) and a subsequent organic material (diazotized aniline hydrochloride) (R. 683; DX-M).

96. As can be seen, the Johannson patent teaches the treating of glass fiber surfaces with hydrolyzable organo silanes which are thereby bonded to the glass surface. The silanes can be alkenyl silanes, including both allyl and vinyl silanes. This patent also teaches the bringing of a coating composition into contact with the treated glass which reacts *in situ* with the silane to directly bond the coating composition to the glass.

97. The Johannson Patent No. 2,557,787 (DX-G, Tab 25) was issued on an application which was a division of the application No. 2,436,304 filed June 11, 1943. This patent being a division, has the effective filing date of June 11, 1943. This patent is specifically directed to a method of "increasing the adhesion of organic resins to glass surfaces" (Col. 1, ll. 35-36). The basis for the invention is described as follows (Col. 1, ll. 37-43):

> "My invention is predicated upon my discovery that siliceous surfaces become organophilic when treated with organosilicon compounds comprising organosilicon halides, and that the adhesion or organic resins to the organophilic surfaces thus provided is substantially greater than it is for the original untreated surfaces."

98. The organo-silicon halides listed by Johannson to be useful include "alkenyl such as methallyl, allyl, etc." (Col. 2, ll. 4-5). The alkenyl includes vinyl silanes (R. 183, 661, 961-62, 1086-87).

99. As to example No. 10, Dr. Rochow explained its importance and states as follows (R. 692):

> "Here, some glass plates had been primed with phenylsilicon trichloride in benzene, and then the excess rinsed away with benzene. A drying oil varnish was then applied to the plates of glass, both treated and untreated, and the plates were immersed in water which was heated to 95 degrees Centigrade. In 18 hours the varnish was free from the unprimed glass but still had good adhesion about 96 hours to the primed glass.
>
> "I should like to point out that drying oil varnish consists of a mixture of liquid olefinically unsaturated polymerizable substances, and that the preferred drying oils contain conjugated double bonds of the type illustrated in the Feiser and Feiser organic books.
>
> "This test provides us with a good illustration of the polymerization of a polymerizable liquid compound to the treated glass surface, said combination by actual test having been fastened much better to the glass surface than the same drying oil varnish applied to unprimed or untreated glass."

100. As pointed out by Dr. Rochow, Johannson used phenyl silicon trichloride in this example. Dr. Rochow demonstrated that phenyl silicon trichloride does in fact have vinyl type unsaturation (R. 794-97). Dr. Rochow concluded that Example No. 10 of the Johannson patent was using a vinyl type unsaturated substance as a coupling agent—a material which reacted with the adsorbed water on the glass surface and established an organo-silane layer which later could bond with the overlying material added on top of the coupling layer (R. 797).

101. The Kropa Patent No. 2,465,731 (DX-G, Tab 20) was issued on an application filed August 1, 1944, and is directed primarily to a method of preparing allyl

chlorosilanes, but its teachings of the properties and uses of those silanes are significant.

102. This patent first describes the method of preparing allyl chlorosilanes and gives three examples of its preparation. It then describes the properties of the silanes and the hydrolysis of the silane to the silicol. It is recalled that hydrolyzed silane—the silicol—is what the defendant utilized to treat glass fibers. The patent specifically teaches that both the silanes and silicols will polymerize "with unsaturated alkyd resins (Col. 5, ll. 51-53). Kropa lists specific resinous materials with which the silicols and silanes will polymerize (Col. 5, l. 57, to Col. 6, l. 3), which include all of the resinous materials used by defendant and its customers.

103. The Kropa patent teaches that the allyl silicols are useful in coating compositions, as adhesives, and in laminating (Col. 6, ll. 4-7). This patent also states (Col. 6, ll. 14-18) that:

> "Since the polymers and copolymers of allyl silicane and the corresponding silicols and silicones adhere to glass very tenaciously, they are particularly useful for glass coating compositions or as adhesives for glass."

As can be seen by this patent, silicols adhere tenaciously to glass, are useful for glass coating compositions and furthermore the silicols are capable of copolymerizing with the very resins used by defendant and its customers.

104. The Steinman Patent No. 2,513,268 (DX-G, Tab 24) was issued on an application filed December 30, 1944, which was filed prior to the filing of the original TeGrotenhuis application and covers an invention made by Dr. Steinman in 1943. This patent teaches the manufacturer of "fibrous glass combined with resinous material or plastics" (Col. 1, ll. 1-3). This patent teaches that one

of the objects is to provide "as an adhesion-promoting agent, substances capable of polymerizing with the resin and reacting with the glass surface of the fibers to create a secure interbond between these dissimilar materials" (Col. 2, ll. 48-53). It states that the invention "provides for increasing the adhesion between resinous materials and glass fiber surfaces by incorporating in the composite material a substance or substances which are effective to promote a strong bond between the resinous materials and the fibers" (Col. 2, l. 54) (Col. 3, l. 4). Steinman teaches the treating of glass fibers with allyl silicates; these allyl silicates are not identical with the materials presently used; however, they are structurally similar and function in the same manner as the allyl silanes and the vinyl silanes (R. 1106-08, 1226-28).

105. In Dr. Steinman's patent, there is described in detail his "double fishhook" or coupling concept, stating (Col. 4, ll. 28-35):

> "The improvements experienced by practice of the present invention are believed due, at least in part, to the fact that the unsaturated silicates are capable of copolymerizing with the resin to become in effect one with the resin surrounding the fiber surfaces. They also are believed to react by hydrolysis with the glass surfaces to be anchored securely to the fibers."

106. The Steinman Patent No. 2,563,288 (DX-G, Tab 26) was issued on an application filed November 13, 1945. Although it was filed about nine months after the TeGrotenhuis 1945 application, it contained a disclosure of glass fibers which was neither disclosed nor suggested by TeGrotenhuis in 1945. Furthermore, the first United States patent filed by TeGrotenhuis relating to any alleged invention concerning glass fibers was not filed until 1951; nearly six years after this Steinman patent.

107. This Steinman patent teaches the use of allyl silanes in place of the allyl silicates (the allyloxy silanes) as the coupling compound and is considered by this Court an extension of the Steinman -268 patent. The mechanism of operation is fully described in the same manner as the previous Steinman patent (Col. 1, ll. 18-31).

> "Although my patent is not to be limited by theoretical considerations, I believe that the improved properties of the laminates produced by my invention may, in part, be explained by the fact that the class of organo-silicon compounds which I use for the pretreatment of the fibrous glass materials are of such molecular structure that they adhere well both to the glass fibers and to the plastic or resin. The silicon portion reacts with and becomes a part of the glass surface and the double bond in the organic radical of the sizing compounds tends to react with the plastic or resin to form a strong chemical union between these two materials which insures a continued strong bond even in the presence of water or moisture."

As can be seen from this patent there is clearly a teaching of interpolymerization between resin and the silane. Furthermore, the evidence shows that Dr. Steinman and Mr. Philipps conceived this invention in 1943, and then proceeded to reduce it to practice (R. 1098-1101, 1141, 1142, 1145-49, 1155-56; DX-RR; DX-CCC). Some glass fibers were treated with the allyl silanes as early as 1943 (R. 11-55-59, 1215-16; DX-TT, p. 319). However, further quantities of allyl silanes could not be obtained until 1945 when commercial production of glass fibers with allyl silanes began (R. 870). The knowledge of Dr. Steinman is clearly prior to the TeGrotenhuis patent. The Steinman patent -288 was conceived in February 1943, and its disclosures were made to Mr. Thomas Philipps, in 1943 (R. 1098-1101, 1141, 1145-49), to Mr. Overman in March or

April 1943 (R. 1142), to Dr. Andregg on June 4, 1943 (R. 1155-56) and to Owens-Corning in a seminar given in April, 1944 (R. 1168; DX-YY; DX-ZZ). Furthermore, Dr. Steinman proceeded to obtain allyl silanes and reduce his invention to practice (R. 1150-51, 1101-04, 889; DX-SS, DX-Y, DX-Z), and when allyl silanes were finally obtained in the summer of 1945, he immediately began using them (R. 1098-1101, 1141, 1142, 1145-49, 1155-56; DX-RR; DX-CCC). Some glass fibers were treated with the allyl silanes as early as 1943 (R. 1155-59, 1215-16; DX-TT, p. 319), however, further quantities of allyl silanes were unobtainable until commercial production of glass fibers treated with allyl silanes began in 1945 (R. 870).

108. The Witt Patent No. 2,649,396 (DX-G, Tab 30) was issued on an application filed on March 17, 1949. This patent teaches the treating of glass fiber with both allyl silanes and vinyl silanes and thereafter applying a polyester resin to the treated fibers and causing the resin to form a bonded structure by *in situ* polymerization (Col. 4, ll. 36-50).

CONCLUSIONS OF LAW.

1. After the -378 patent issued, an interference was declared by the Patent Office between the claims in the -378 patent and the claims in a patent filed by Luther S. Yaeger of Bjorksten Laboratories. The plaintiff has made references to this decision as holding that Mr. TeGrotenhuis is entitled to the benefit of the 1945 filing date of his patent. Upon review of this case, TeGrotenhuis v. Yaeger, 290 F.2d 951 (C.C.P.A. 1961), this Court finds that this interference proceeding was directed to one specific issue, namely, whether or not Mr. TeGrotenhuis's 1945 application contained a sufficient disclosure of vinyl silanes to entitled him to the benefit of the 1945 filing date

for claims directed to vinyl silanes. In the Court's opinion, reversing the Patent Office Board of Interferences, it held that the 1945 application did contain a sufficient disclosure of vinyl silanes. This Court accepts the opinion of that Court, however, its holding is narrow and contains nothing concerning other features of the -378 patent which Mr. TeGrotenhuis relies upon to gain the benefit of the 1945 filing date. As has been pointed out previously, this Court is concerned with whether or not there was a disclosure of glass or glass fibers in the 1945 application which could give the plaintiff the benefit of the 1945 filing date for that claim. Also this Court is concerned with the disclosure of the superiority of vinyl silanes over other silanes, notably allyl silanes, which would entitle him to the benefit of the 1945 application for claims concerning that issue. The Court of Customs and Patent Appeals did not have before it, nor did it speak or determine the sufficiency of the 1945 application in view of the failure thereof to teach a method whereby the vinyl silanes could be made, nor did the Court consider or speak of the relevant prior art.

[1] 2. For a patent to issue, there must be the requisites of novelty, utility and invention. Allied Wheel Products v. Rude, 206 F.2d 752 (6 Cir., 1953); United States Gypsum Co. v. Consolidated Expanded Metal Companies, 130 F.2d 888 (6 Cir., 1942) cert. denied 317 U.S. 698, 63 S.Ct. 441, 87 L.Ed. 558.

3. In Great Atlantic & Pacific Tea Co. v. Supermarket Equipment Corp., 340 U.S. 147, 152-153, 71 S.Ct. 127, 130, 95 L.Ed. 162 (1950), the Court states;

> "The conjunction or concert of known elements must contribute something; only when the whole in some way exceeds the sum of its parts is the accumulation of old devices patentable * * * The func-

tion of a patent is to add to the sum of useful knowledge * * * A patent for a combination which only unites old elements with no change in their respective functions, such as is presented here, obviously withdraws what already is known into the field of its monopoly and diminishes the resources available to skillful men."

See also Lincoln Engineering Co. v. Stewart-Warner Corp., 303 U.S. 545, 549-550, 58 S.Ct. 662, 82 L.Ed. 1008 (1938).

4. In Electric Vacuum Cleaner Co. Inc., v. P. A. Geier Co., 118 F.2d 221, 224 (6 Cir., 1941), that Court pointed out that;

"It's not sufficient that a thing is new and useful to entitle its creator to a patent. He must do more. He must discover it by either mental labor or intellectual creation, although it may be the result of mental accident. It cannot arise from knowledge common to all persons skilled in the art. The patentee must have some addition to the common stock of knowledge and not be merely the first to use in combination what was known before, without producing a new and different result."

See also Westinghouse Electric & Manufacturing Co. v. Powerlite Switchboard Co., 142 F.2d 965 (6 Cir., 1944).

5. In Schriber-Schroth Co. v. Cleveland Trust Co., et al., 305 U.S. 47, 57, 59 S.Ct. 8, 83 L.Ed. 34 (1938), the Court stated:

"It follows that the patent monopoly does not extend beyond the invention described and explained as the statute requires, Permutit Co. v. Graver Corporation, supra, 284 U.S. 52, at page 57, 52 S.Ct. 53, [76 L.Ed. 163], that it cannot be enlarged by claims in the patent not supported by the description, Snow v. Lake Shore & M. S. Ry. Co., 121 U.S. 617, 7 S.Ct. 1343, 30 L.Ed. 1004; cf. Smith v. Snow, 294 U.S. 1, 55 S.Ct. 279, 79 L.Ed. 721, and that the application

for a patent cannot be broadened by amendment so as to embrace an invention not described in the application as filed, at least when adverse rights of the public have intervened."

See also Chicago Forging Mfg. Co. v. Bade-Cummins Mfg. Co., 63 F.2d 928 (6 Cir., 1933).

[2] 6. Upon consideration and review, this Court finds that the evidence presented at trial conclusively shows that the plaintiff's allegations of infringement are naked and unsupported by the requisite facts, and that the heavy burden of proof that is necessary to invalidate the plaintiff's patents in the suit has been amply met by the defendant, and their affirmative defense that the patents -378 and -566 are invalid, void and not infringed upon is sustained by this Court.

7. With respect to alleged infringement, it is the finding of this Court that the defendant's practices regarding three vinyl silanes and a methacrylato silane are not the teachings of either of the TeGrotenhuis patents in suit.

8. The defendant does not utilize allyl silanes in its practices, as the -566 patent states, nor does it apply the coupling compounds either by a vapor treatment or from an organic solvent as the TeGrotenhuis patent states. Rather the defendant applies all the coupling compounds to the glass fibers from water solutions.

9. The fourth silane, the methacryloxypropyltrimethoxysilane (A-174 and Z-6030) is neither a vinyl or allyl silane, nor an alkenyl silane (R. 800-01, 962-68, 1020). This particular silane, not being a vinyl silane nor an equivalent of vinyl is not within the scope of the -378 or -566 patent.

10. For these reasons, the practices of the defendant are not within the plaintiff's allegations of infringement, and are not considered by this Court.

11. As a matter of law, this Court finds that the prior art relevant to this case shows that organo-silanes react with glass surfaces, including fiber glass surfaces and thereby become bonded to the glass. Also, the prior art teaches specifically that alkenyl silanes (which include both allyl and vinyl) react with glass surfaces and become bonded thereto. It is noted that the prior art teaches that the alkenyl silanes promote adhesion of resins to fiber glass. The alkenyl silanes and specifically the allyl silane when adhered to glass and glass fibers, will chemically react with a subsequent coating composition to bond the coating to the glass. Furthermore, the prior art also teaches that the allyl silanes will copolymerize with the polyester resins involved in this suit. In view of these findings, this Court concludes that Mr. T. A. TeGrotenhuis made no contribution to relevant art involved in this suit. For these reasons, the subject matter of the patents in suit was obvious to those skilled in the art at the time of the alleged TeGrotenhuis invention. Pursuant to 35 U.S.C. § 103 the patents are invalid, and this Court so finds.

12. Furthermore, the original 1945 application of T. A. TeGrotenhuis neither discloses or relates to any suggestion of glass or glass fibers. Therefore, this Court will give no validity to claims in a subsequent application covering glass or glass fibers based upon the 1945 application.

13. Furthermore, the 1945 application fails to teach any method of making a hydrolyzable vinyl silane. It is again stated that no method was known of making such a material in 1945 by those skilled in the art. It is concluded therefore that the 1945 application is invalid as to claims of a vinyl silane.

14. Also the 1945 application does not teach that vinyl silanes are superior in any respect to other silanes. It is the finding of this Court that the -378 patent is predicated solely on this alleged superiority and therefore is not entitled to the filing date of the defective 1945 application.

15. The allyl and the vinyl silanes are homologues and admittedly equivalents.

16. The use of allyl silanes has been amply demonstrated and fully disclosed in the prior art, thus invalidating the -566 patent.

17. No new or unexpected results are achieved by the use of vinyl silanes as distinguished from the allyl silanes of the prior art when used for treating glass fibers for use in the reinforcement of polyester resins.

18. For these reasons, the TeGrotenhuis patents -566 and -378 are not entitled to the 1945 application filing date. Therefore, the United States Patent No. 2,742,378 granted April 17, 1956 and United States Patent No. 2,841,566 granted July 1, 1958 are declared invalid.

19. It is the finding of the Court that the evidence conclusively shows that Dr. Steinman and his colleagues at Owens-Corning had conceived all essential features of the subject matter claimed and had applied all essential features of the subject matter claimed and had applied both allyl silicates and allyl silanes to glass fibers before any date of invention alleged by Mr. TeGrotenhuis. This invention of the subject matter having been made by Dr. Steinman and known to him and his co-workers before Mr. TeGrotenhuis conceived his alleged invention renders the TeGrotenhuis patents invalid in accordance with 35 U.S.C. § 102(a) and (g).

20. Upon careful review of the records, and as pointed out, this Court concludes that all essential features of the subject matter claimed in the two patents were taught to Mr. TeGrotenhuis by Dr. Rochow. Therefore, pursuant to 35 U.S.C. § 102(f) the patents in suit are invalid due to lack of invention.

21. Therefore, judgment is entered for the defendant, Owens-Corning Fiberglas Corporation, and the patents of T. A. TeGrotenhuis applicable to this suit are hereby declared invalid and not infringed by the defendant.

22. This constitutes the findings of fact and conclusions of law pursuant to Rule 52(a) of the Federal Rules of Civil Procedure.

APPENDIX E.

PATENTS IN CONTROVERSY.

(Attached.)

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United States Patent Office 2,742,378 Patented Apr. 17, 1956

2,742,378

FILLERS HAVING VINYL SILOXANE GROUPS BONDED TO THE SURFACE THEREOF AND COPOLYMERS THEREOF WITH ETHYLENICALLY UNSATURATED POLYMERIZABLE MONOMERS

Theodore A. Te Grotenhuis, Olmsted Falls, Ohio, assignor of twenty per cent to The General Tire & Rubber Company, Akron, Ohio, a corporation of Ohio

No Drawing. Application August 2, 1952, Serial No. 302,415

28 Claims. (Cl. 117—76)

This application is a continuation-in-part of my application Serial No. 251,152, filed October 12, 1951, and of my application Serial No. 243,737, filed August 25, 1951, and of my application Serial No. 585,824, filed March 30, 1945, now abandoned, which application was copending with application Serial No. 593,970, filed May 15, 1945, now abandoned, and with application Serial No. 559,848, filed October 31, 1944, now Patent 2,457,097, which is a continuation-in-part of application Serial No. 424,293, filed December 26, 1941, now abandoned.

The present invention relates to composite articles of reinforcing material such as pigments and fibers, preferably a matted or woven fabric, and a high molecular weight polymeric substance. It particularly relates to composite articles and methods of preparing such articles comprising a water insoluble inorganic pigment or textile fabric or fibers and in situ polymerized high polymer molecularly bonded to said fabric by interaction of unsaturated linkages on the fiber or pigment surface and of the monomer entering into the solid polymer. The term "polymer" is herein used in its generic sense to include copolymers of one or more monomers.

Composite articles of pigments such as silica, titania, carbon black, etc. and/or fibers such as cellulosic fibers, glass fibers, and the like, and a high polymer such as a polymer of a material comprising a mono-olefinic compound such as styrene, methyl methacrylate, vinyl halide, etc. as a substantial polymerizing ingredient thereof are well-known. Such composite articles in which the pigments, fabric or fibers act as reinforcing agents which should contribute great strength and impact resistance to the article sometimes have relatively low water resistance or the bond between the water insoluble pigment or fiber and the resin is insufficient to prevent rupture when contacted with certain fluids. The strength of the composite article may also be much less in the dry state than should be the case if proper adhesion of fiber and polymer were obtained. Even thermoset or cross-linked polymers reinforced with fibers and pigments are frequently adversely affected. The result is to limit the utility of the composite article.

It is an object of the present invention to provide reinforced articles of any textile fabric and a high polymeric material formed of a monomer having polymerizable olefinic unsaturation, in which the bond between the fabric and the high polymer may be chemical in nature and therefore much stronger than the usual adhesive forces.

It is another object of the present invention to provide a textile fabric which, when treated with free radical polymerizable mono-olefinic monomers or mixtures comprising such monomers can form interlocking chemical bonds therewith.

It is another object of the present invention to provide a method of treating fine particles such as pigments, fibers, and fabrics so that they are readily compounded with organic substances and so that they can be bonded thereto

by chemical means such as by possible interpolymerization or by sulfur or chemical bridges.

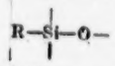
It is another object of the present invention to provide a method of treatment for fine particles and fibers by which the particles are rendered more readily wettable and interlocked with polymerizable organic compounds and polymers.

It is still another object of the present invention to provide a simple and inexpensive method of improving the ease of dispersion and compounding of fine particles in organic vehicles and polymers.

It is a further object to provide composite articles and a method of making composite articles comprising a solid polymer of a free radical polymerizable unsaturated material reinforced with textile-fabric and having the textile fabric molecularly interlocked with said solid polymer. Other objects will be apparent from the following description of the invention.

In accordance with the present invention, an olefinic siloxane, preferably a vinylsiloxane, is deposited on the surface of the fabric. This is most conveniently accomplished by subjecting the surface of the fabric to contact with a water reactive organosilicon compound containing at least one organic group having aliphatic carbon-to-carbon double bonds, preferably a vinyl group, at least one group split off together with H from contacting —OH to form a new silicon-oxygen bond. The organo silicon compounds generally have the general formula

where X is a group which is split off with hydrogen from contacting hydroxyl groups with formation of a new silicon-oxygen bond. X is preferably chlorine or bromine, although it may be oxyaryl, oxyaliphatic, or amino (NH_2 groups). R is an unsaturated group preferably an unsaturated hydrocarbon group. Examples of suitable unsaturated groups are dienyl, and the vinyl groups, vinyl, chlorvinyl, and bivinyl, and Y and Z may be selected from any monovalent organic groups, preferably those hydrocarbons with less than 7 carbon atoms such as phenyl, methyl, etc., and groups split off by contact with hydroxyl groups and oxygen-containing groups. This treatment provides on the surface of the fibers the



groups where the free silicon valences are attached to oxygen or carbon and the free oxygen valence is generally attached to the surface of the fiber or pigment. Those compounds having a carbon-to-silicon bond are preferred because of their increased stability at elevated temperatures.

Examples of suitable hydroxyl or water-reactive organosilicon compounds having unsaturated groups for interaction with in situ free radical polymerizable monomer containing compositions are the water hydrolyzable alkylenyl silicon halides including the mono-, di-, and tri-vinyl silicon chlorides, bromides, and amines all of which may be seen to have a carbon of a carbon to carbon double bond connected directly to silicon. The haloalkylenyl silicon chlorides and bromides, the dienyl silicon chlorides and bromides such for example as the butadienyl silicon chlorides and bromides all of which have at least one organic group with at least two carbon atoms connected by double bonds. Vinyl and butadienyl groups with less than 6 carbon atoms are preferred because of the usual greater polymerization activity of these groups. If, more than one organic group is attached to silicon, only one need be unsaturated to enter into the

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copolymerization with the monomer. Thus, the alkylenyl alkyl silicon chlorides such as dimethyl vinyl silicon chlorides, and dimethyl isopropenyl silicon chlorides are suitable. When more than one unsaturated group is present, these unsaturated groups need not be the same. For example, vinyl allyl silicon chlorides and bromides and amines may be used. Similarly, the halogen alkylenyl silicon chlorides and bromides such for example as chlorvinyl dimethyl silicon chlorides and others having a chlorine containing unsaturated group, and attached directly to silicon a group hydrolyzable or reactive with water or hydroxyl particularly adapted to split out halogen present as HCl or the NH_2 as ammonia and form a new silicon-oxygen bond are suitable for the fabric treating step in the course of the present invention. Even partially condensed (liquid) vinyl siloxanes (i. e. the hydrolysis products of vinyl chlorsilanes) appear to be water hydrolyzable or reactive to hydroxyl to shift oxygen and form a new silicon-oxygen bond to the surface of the pigment or fiber.

Although the present invention is not concerned with the preparation of the unsaturated water reactive silicon compounds per se, the organosilicon compounds which contain a group which is split off by reaction with water because of extreme desire of silicon to form a new silicon-oxygen bond and which contains an alkylenyl or aliphatic unsaturated group attached to the silicon atom may be prepared in any suitable way as by one or more of the previously proposed following methods.

(A) The Grignard synthesis wherein the desired organohalide as for example R—Br where R is the desired organic radical such for example as vinyl, etc., with silicon tetrachloride or a mono- or diorgano substituted silicon tetrachloride in the presence of magnesium, etc. the conditions for Grignard reactions are well-known in the art.

(B) By cracking at elevated temperatures the corresponding saturated compounds in the presence of a dehydrogenation catalyst to split off hydrogen, for example, ethyl silicon chlorides may be converted to vinyl silicon chlorides by this well-known process.

(C) In some cases they may be prepared by reaction of an unsaturated hydrocarbon such as acetylene, etc. with a silicon tetrachloride or hydride in the presence of a suitable catalyst.

The preparation or properties of organo-substituted silicon halides (organohalo silicones) is well-known and is set forth in one or more of the following United States patents:

Lincoln et al. 2,129,281
Nason 2,182,208
Rochow 2,258,218–19–20–21–22
Rochow 2,286,763
Rochow 2,352,974
Hyde 2,371,050
Rochow 2,371,068

The reinforcing such as the pigment, textile fabric, or other fibrous material used as reinforcing in the composite articles formed in accordance with the present invention is treated by simply contacting the dry fabric with the hydroxyl or water hydrolyzable or condensable silicon compound such as the vinyl silicon chlorides, vinyl silicon amines, vinyl silicon hydroxide, etc. Any method of effecting contact either vapor phase or liquid may be used. The one or more of the reactive silicon compounds (at least those which are relatively non-volatile) are preferably admixed in solution in a non-reactive solvent such for example as a hydrocarbon liquid such as benzene, toluene, or any other diluent that does not react with the silicon halides or amine used. The silicon compound is preferably present in small proportions in the solvent such as .1% to 5% although the reactivity of silicon is such that the extremely dilute solutions are effective. When the silicon compound is liquid, the substantially pure liquid may be used although a dilute solution is

more desirable. The reactive silicon compound apparently reacts with hydroxyl or carboxyl groups chemically absorbed or combined with the surface of the fabric to provide unsaturated groups such as vinyl, etc., groups attached over the surface thereof through silicon atoms which are highly compatible with olefinic polymerizable materials and which are capable of chemically combining into the molecules formed by the polymerization of such materials. As before mentioned, the unsaturated groups in the silicon compound may have many carbon atoms, but those having four carbon atoms or less for each unsaturated group and particularly those having less than three carbons per double bond, namely the vinyl and butadienyl silicon halides are preferred. This is especially the case when the reinforcing pigment or fiber is to be used in preparing composite articles by a method wherein a monomeric styrene is subjected to polymerization in contact with the reinforcing fiber or pigment. The olefinic group in such vinyl siloxanes is apparently much more active to interpolymerization than when 3 or more carbons per olefinic group are present. The fibers, fabrics and pigments treated with the solution should be dry and free from water so that reaction with water and hydroxyl not chemically combined or held on the surface of the fibers is avoided. The treated fabric may be neutralized, heated, or washed to eliminate or vaporize traces of acid or ammonia, alcohol, etc. or product split off by reaction or these materials may be volatilized therefrom.

In accordance with the present invention, the fabric which has been treated as above is contacted or immersed in a composition comprising a polymerizable olefinic compound and preferably a polymerizable mono-olefinic compound of less than 6 aliphatic carbon atoms and capable of polymerizing by free radical initiators such as a peroxide and hydroperoxide catalyst, and the polymerizable olefinic compound is subjected to catalyst and caused to polymerize and cause to set to the solid state while in contact with the treated fabric whereby interaction of double bonds on fabric and monomer occur to build the fabric chemically into the solid molecule. The monomer preferably contains other ingredients such as a polyester, such as the condensation product of a glycol, maleic anhydride and phthalic anhydride, or diallyl phthalate, etc. or polystyrene, etc.; dissolved therein to interpolymerize or to interact in forming the solid polymer. When a solution in its monomeric polymerizable material of a resinous polymer such for example as polystyrene, polymethyl methacrylate, polymethyl acrylate, polyvinyl ester, polyamine, or other organic polymerization or condensation product is applied to the surface of the treated fabric and the solvent caused to polymerize insitu a more adherent coating may be had to the fabric and a direct chemical union between the fibrous material and the polymerizable or dissolved constituents is usually obtained.

Examples of the most commonly used free radical initiators or catalysts are benzoyl peroxide, cumene hydroperoxide, tertiary butyl hydroperoxide, and other organic peroxides and hydroperoxides. The peroxide, as is well-known, is usually used in relatively small amounts such as 1 to 2% of the weight of the polymerizable ingredient, such for example as the monomeric styrene present. Any of the various free radical initiators may be used when soluble or usable in one of the liquids of the method of polymerization used.

The temperature of polymerization is generally dependant on the size of the articles produced and the amount of catalyst present, it being necessary to remove the heat of polymerization. Higher temperatures increase polymerization speed, and cause greater exothermic reaction and may be used in thinner and smaller articles. The polymerization temperature is usually within the range of 50° F. to 200° F. and should be well below the boiling point of monomers present at the pressure used.

The following examples illustrate the present invention.

Example 1

A dry, glass fabric which has been previously freed from sizing and dried at 100° C. in a vacuum oven is submerged in a solution in 100 parts of dry toluene of five parts of a mixture of vinyl silicon chlorides having one to three vinyl groups attached directly to silicon and the remaining valences attached to chlorine. The fabric is allowed to stand in the solution for a few minutes, removed and drained free of liquid, and dried in a 75° C. vacuum oven to remove all traces of hydrochloric acid. The thus treated fabric is thereupon immersed into a styrene solution comprising 60 parts of styrene and 40 parts of a polyester prepared by condensing about 30 mol parts of maleic anhydride with 70 mol parts of adipic acid and 102 mol parts of ethylene glycol until a relatively viscous material is obtained, boiling at least 250° C. In effecting the condensation, the ingredients are heated slowly at first under an inert gaseous atmosphere, for example N_2,Co_2 etc., and the amount of heat applied is merely sufficient to cause vigorous boiling. As the reaction progresses, with elimination of water the temperature rises until a temperature of about 250° C. is obtained. The styrene solution of the polyester is mixed with one part of cumene hydroperoxide as a free radical initiating catalyst and is maintained at slightly elevated temperatures under an atmosphere of nitrogen and with oxygen excluded until a hard solid article is produced having the fabric insitu and intimately bonded through the now polymerized unsaturated linkages to the solid copolymer thus obtained.

Example 2

When several sheets of fabric are wetted as in Example 1 with the solution of unsaturated polyester in styrene and the wetted sheets plied up and pressed against each other and allowed to so remain until the polymerization progressed to the solid state, a laminated structure having exceptionally desirable properties is obtained.

Example 3

In place of the polyester-styrene solution of Example 1, a solution of polystyrene in styrene monomer and having about the same viscosity is substituted, other conditions being the same. An article having fabric bonded to the in situ polymerized polymer is also obtained.

Example 4

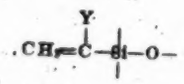
The styrene polyester solution of Example 1 is substituted by a viscous solution of polymethylmethacrylate in methacrylate monomer and the polymer, monomer, fiber mixture thus obtained is allowed to polymerize in shape form as in Example 1, except that the temperature was raised to about 80° C. and the catalyst was substituted by 1% based on the weight of the monomer present of benzoyl peroxide, other conditions being the same. A shaped article having fabric or fiber intimately bonded insitu is also obtained.

The vinyl silicon halides in the above examples may be substituted by any one or more of butadiene silicon halides, other materials capable of depositing vinylsiloxane units adherently on the surface of the reinforcing material, and vinyl silicon amines to also produce an integrally bonded composite article having excellent properties. Also as described and claimed in my related application Serial No. 251,152, filed October 12, 1951, vinyl isocyanates and other unsaturated isocyanates and isothiocyanates having a carbon-to-carbon double bond capable of entering into copolymerization may also be used in place of the unsaturated silicon halides to also obtain desirable properties in the fiber reinforced plastic or solid polymer article. The glass fabric may be substituted for matted glass fibers and other textile fabrics including cotton, rayon, and the like having oxygen containing hydroxyl groups (which of course are present in carboxyl groups) on surface portions thereof. The fabric or fibers in each instance being bonded to the insitu polymerized polymer by interaction of the unsaturated groups and the surface thereof with the monomer during the polymerization thereof. The solution containing the polymerizable monomer of the above examples may be substituted by other monomers or mixtures comprising monomers polymerizable as by homopolymerization copolymerization, or interpolymerization to the solid state by free radical mechanism.

Example 5

100 grams of unbeaded carbon black are subjected to agitation in the presence of about one gram of a saturated vapor of a mixture of allyl dimethylsilicon chloride and methyl diallylsilicon chloride, the presence of saturated vapor being insured by a reducing of the pressure and elevating the temperature in the container. The agitation is continued in the presence of the organo-silicon halide vapor for about 10 minutes to allow thorough penetration of the vapor through the carbon black. The hydrochloric acid formed by the reaction is removed in any suitable manner, as for example vaporization at elevated temperature by neutralizing with an alkali material such as dry NH_3, by shaking the carbon black with water, or preferably by treating the carbon black with ether and water and washing the carbon black ether mix until free from acid. The carbon black thus treated has much less tendency to be wet by water and much greater tendency to be wet by hydrocarbon organic solvents and contains allyl groups attached thereto for interpolymerization with free radical polymerizable materials, such as diallyl phthalate and the like.

The pigments in the above example may be substituted by other finely divided pigments including silica, aluminum oxide, titanium oxide, and the like, as well as fibers. The silicon halide may be substituted by the other unsaturated organosilicon compounds such as the vinylhalosilanes including vinyl trichlorsilane, bivinyl chlorsilane, divinyl dichlorsilane, and trivinyl monochlorsilane and mixtures of the same to obtain vinylsiloxane groups (vinyl siloxane portions of hydrolysis products of a vinyl chlorsilane) of the formula



(where Y is hydrogen or halogen and the free silicon bonds are attached to carbon and/or oxygen atoms) on the surface of the silica, carbon black, fiber, and the like, which may be more readily interpolymerized with the highly activated polymerizable monomers such as styrenes (including styrene, vinyl toluene, etc.), methyl methacrylate, butadiene, and the like, which monomers are characterized by having a double bond in conjugated relation with the polymerizable olefinic double bond for resonant activation thereof.

Example 6

5 parts of carbon black treated as in Example 1 are dispersed into 100 parts by weight of styrene containing about ½ part of benzoyl peroxide and ½ part of soya lecithin by passing the mixture through a colloid mill. The dispersion thus prepared is then strongly agitated into a mass of water to maintain a suspension (fine droplets of styrene throughout the aqueous phase). The aqueous fluid is maintained in a completely filled vessel under superatmospheric pressure for several hours with said agitation until polymerization of the styrene in suspended form is had. The polystyrene thus produced has an unusual degree of jetness and it is desirable for use as a molding powder and in the preparation of plastic articles, or for solution in the preparation of a coating composition.

Example 7

The styrene in Example 6 is substituted by an equal amount of methyl methacrylate. The water of Example 6 is also substituted by an equal amount of a 1% aqueous solution of polymethacrylamide, other conditions remaining the same. The polymethyl methacrylate thus produced has exceptionally desirable properties.

Example 8

100 grams of finely divided silica treated as was the carbon black in Example 5 with saturated vapor of a mixture of mono-, di-, and trivinyl chlorsilanes to provide vinyl siloxane units on the surface of the silica are dispersed in a fluid comprising a solution of 10 parts of polystyrene in 90 parts of monomeric styrene and containing about one part of benzoyl peroxide. The mixture thus obtained is suspended as fine droplets in a mass (about 500 parts) of water containing about 1% of polymethacryl amide. The agitation is continued in a completely filled vehicle under superatmospheric pressure and with constant agitation at about 80° C. until the styrene is polymerized. The molding powder having polystyrene bonded to the silica through the residue from the interaction of the vinyl siloxane units and the styrene is obtained.

Example 9

The fluid in the above example containing monomeric styrene is substituted by an equal amount of a solution of polymethyl methacrylate in methyl methacrylate monomer other conditions remaining the same. A similar result is had.

When in the preceding examples, the aqueous solution is eliminated, a mass polymer is obtained upon polymerization of the polymerizable solvent (monomer) of the solution of resinous polymer in monomeric polymerizable material. The polymerization may or may not be in shaped form to form a shaped article directly as desired. The silica in the above example may be substituted by other pigments and fibers including glass fiber, rayon, cotton, and cellulose fibers having vinylsiloxane units attached to their surface as above noted.

Example 10

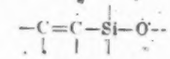
100 grams of matted glass fiber are contacted with 100 grams of a 10% solution in anhydrous benzene of vinylisocyanate at slightly elevated temperature. The treated fiber is then drained and allowed to dry. The fibers are maintained in contact with the isocyanate for approximately 15 minutes. These fibers are then wetted with a polymerizable polyester compound comprising one part of benzoyl peroxide, 200 parts of monomeric styrene, and 200 parts of a syrupy condensation product of 100.2 mol parts of ethylene glycol or diethylene glycol, 80 mol parts of phthalic acid anhydride, and 20 mol parts of maleic anhydride. The wetted fibers are molded and allowed to set up in the mold in the usual manner. The resulting compound is found to have increased water resistance and strength compared to compounds made from untreated glass fibers.

In this example, other textile fibers such as cotton and rayon fibers may be substituted for the glass fibers.

While the present invention is obviously especially applicable to the preparation of composite articles comprising a plurality of layers of fabric adhered together, it is also applicable to cast articles containing fibrous material therein as a reinforcing agent and to all fabrics having a coating formed by in-situ polymerization of an unsaturated material. The free radical mechanism of polymerization is preferred, but the ionic, or acidic polymerization mechanisms such as utilized by the so-called alfin catalytic process of polymerization or the Friedel-Crafts process of polymerization wherein a Friedel-Crafts or alfin catalyst or even a sodium catalyst is used in place of the free radical producing alkyl peroxide is also applicable.

The monomeric materials used in the present invention are those containing polymerizable olefinic double bonds preferably in conjugation with a second olefinic double bond or other double bond which may resinate therewith. These monomeric materials include vinyl chloride, vinylidene chloride, vinylacetate, butadiene, isoprene, chloroprene, and other diolefinic compounds of less than 7 aliphatic carbon atoms, acrylonitrile and methacrylonitrile, methyl methacrylate, and other methacrylates and acrylates, arylvinyl compounds, and halogenated arylvinyl compounds such as the nuclearly chlorinated styrene, fluorinated styrenes, trifluoryl methyl styrenes, and the alphamethyl styrenes which are not substituted in the 2 and/or 6 position of the nucleus, or in the beta position of the side chain. Any one or more of the materials may be present in the polymerizable mixture.

The term "pigments" is used herein and in the appended claims in the generic sense as generally used by rubber compounders and the like to include powders, fillers and pulverulent inorganic solids generally regardless of whether they have as does carbon black and titanium dioxide, high coloring value, or have like silica and glass, no appreciable coloring value. Inasmuch as the hydrolysis products of an organohalosilane as is well known condense with hydroxyl on the surface of a solid or of other hydrolysis products to split out water which has no function, the terms "unsaturated siloxane portion of a hydrolysis product" and "vinyl siloxane portion of a hydrolysis product of a halosilane" are used in the appended claims to designate the active portion of the hydrolysis product, namely the previously mentioned group having general structural formula



wherein the free silicon valences are connected to oxygen or carbon and the free carbon valences are connected to hydrogen, halogen or carbon. These terms do not include the portions of the hydrolysis product which are split off by condensation with other hydrolysis product or with hydroxyl on the surface of the solid to form water.

In my application Serial No. 439,463, filed June 25, 1954, I disclose and claim composite articles comprising textile fibers and/or inorganic pigments or powders with unsaturated organosiloxane groups bonded to their surfaces, which unsaturated organosiloxane groups are characterized by having olefinic groups spaced from the silicon by one carbon atom only.

It is to be understood that in accordance with the provisions of the patent statutes, variations and modifications of the specific examples herein described for purposes of illustration may be made without departing from the spirit of the invention.

What I claim is:

1. A member of the group consisting of fibers and inorganic pulverulent solids, which normally have hydroxyl groups on the surface thereof but which are modified by having unsaturated aliphatic siloxane groups, with a carbon of a carbon-to-carbon double bond directly attached to silicon, attached to surface portions thereof whereby said group members are capable of forming a chemical bond by in situ interaction with a contacting olefinic polymerizable material, said surface portions containing said unsaturated siloxane groups being different from the interior of said group members and being an unsaturated siloxane portion of a product from hydrolysis of a halosilane having all valences of the silicon atom thereof connected to hydrocarbon and halogen groups, whereby after reaction with hydroxyl all valences of silicon are connected to a member of the group consisting of carbon and oxygen atoms, the unsaturated aliphatic groups of said unsaturated aliphatic siloxane groups being attached to said group member through silicon-oxygen linkages.

2. A product according to claim 1 wherein the unsaturated aliphatic groups are bivinyl groups.

3. An article of manufacture comprising a member of the group consisting of fibers and inorganic pulverulent solids and a solid in situ polymerized synthetic organic polymer of a liquid olefinic compound and an interfacial layer on said member of said group and in contact with said solid polymer, said layer comprising the residue from the interaction of vinyl siloxane groups on said group member with said groups in said polymerizable liquid which react with olefines, vinyl groups of said vinyl siloxane groups on said group member being attached directly to silicon, said surface layer on said group member prior to polymerization being vinyl siloxane groups and being different from the body of said group member and from said synthetic organic polymer, said group member prior to adhering vinyl siloxane groups thereto normally having hydroxyl groups on the surface thereof.

4. A method of forming an article comprising a member of the group consisting of inorganic pulverulent solids and fibers bonded together by a resinous polymer, which comprises wetting said group member with a polymerizable liquid comprising a monomeric polymerizable styrene and causing polymerization of said monomeric styrene in contact with said group member to form a solid while in contact with said group member, said group member normally having hydroxyl groups on the surface thereof but being characterized by having attached to surface portions thereof a coupling compound comprising a group of the formula

where the free valences of the silicon are attached to a member of the group consisting of oxygen and carbon atoms, said coupling compound, the body of said group member and the body of said resinous polymer being different.

5. A method of forming a composite article which comprises wetting an inorganic solid with olefinic polymerizable liquid capable of setting to the solid state and having groups which react with olefine groups, said inorganic solid having attached to the surface thereof vinyl siloxane portions of hydrolysis products of a vinyl halosilane having only vinyl and halogen groups attached to silicon.

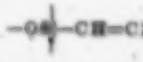
6. An inorganic solid having attached to surface portions thereof a vinyl siloxane portion of hydrolysis products of a vinyl halosilane having only vinyl and halogen groups attached to the silicon atom thereof.

7. An article of manufacture comprising (1) a member of the group consisting of fibers and inorganic pulverulent solids, which normally have hydroxyl groups on the surface thereof but which are modified by having a surface layer of polymerizable unsaturated aliphatic groups which have a carbon of a carbon-to-carbon double bond attached directly to silicon, said groups being attached to the surface of said fibers through silicon-oxygen linkages, and (2) a contacting in situ polymerized solid polymer of a styrene, said solid polymer being bonded to said fibers by polymerization of said styrene with said unsaturated aliphatic groups, said surface layer being different from the body of said member of said group.

8. Reinforcing materials which are suitable for in situ polymerized high polymers of olefinic compounds, said reinforcing materials being selected from the group consisting of fibers and pigments, the surfaces of which normally have hydroxyl groups on the surface thereof but which are modified by having attached thereto vinyl siloxane units in which the vinyl groups are attached through siloxane groups, whereby interpolymerization of the vinyl siloxane and a resonantly-activated liquid polymerizable olefinic material may be had.

9. A method of forming an article comprising a member of the group consisting of fibers and inorganic pulverulent solids, which normally have hydroxyl groups on the surface thereof but which are bonded together by a resinous polymer, which comprises wetting said group member, surface portions of which are modified by a contacting interface comprising bivinyl groups attached to silicon, with a polymerizable liquid comprising monomeric styrene, and causing polymerization of said monomeric styrene in contact with said group member to form a solid while in contact with said group member, said interface and the body of said group member being different, said bivinyl groups being attached to said group member through silicon-oxygen linkages.

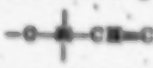
10. A method of forming an article comprising a member of the group consisting of fibers and inorganic pulverulent solids, which normally have hydroxyl groups on the surface thereof but which are bonded together by a resinous polymer, which comprises contacting surface portions of said group member with a vinyl chlorosilane to modify surface portions thereof and attach groups of the general formula



thereto, wetting the treated surface of said group member with a polymerizable liquid comprising a free radical catalyzed monomeric polymerizable liquid olefine having two sets of double bonds, and causing polymerization of said olefine in contact with said group member to procure a solid body.

11. A method of forming an article comprising a member of the group consisting of fibers and inorganic pigments, bonded together by a resinous polymer, said method comprising wetting said group member which normally carries hydroxyl groups on the surface thereof, but which has surface portions thereof modified by having vinyl groups attached thereto through silicon of a silicon-oxygen linkage, all valences of said silicon atoms being attached to a member of the group consisting of carbon and oxygen, at least one valence being connected to carbon and at least one valence of said silicon being directly connected to oxygen, with a liquid comprising a liquid polymerizable olefinic monomer of said polymer, and causing polymerization of said monomer to the solid state while in contact with said group member, said surface portions and the body of said group member being different.

12. An article of manufacture comprising an inorganic pigment, the particles of which normally carry hydroxyl groups on their surfaces but which have the surfaces modified by having attached thereto groups of the formula



where the free silicon valences are attached to atoms selected from oxygen and carbon, said groups attached to said pigment being different from the body of said pigment, and said pigment particles being bonded together by an in situ polymerized solid polymer deposited from a liquid comprising a monomeric polymerizable olefinic compound, said solid polymer being in contact with the said groups on the surface of said particles.

13. The article according to claim 12 wherein the polymer is a polymer of a liquid comprising a monomeric styrene.

14. A material suitable for wetting by a polymerizable material and to be bonded thereto during subsequent in situ polymerization, said material being selected from the water-insoluble members of the group consisting of fibers and inorganic pigments, the surfaces of which normally carry hydroxyl groups on the surface thereof but which are modified by having attached thereto vinyl siloxane units, the vinyl groups being attached through the silicon-oxygen linkage, whereby interpolymerization of the vinyl siloxane and a liquid polymerizable olefinic material may be had, the amount of vinyl siloxane on said group member being small compared to the amount

of said liquid polymerizable olefinic material required to fill the voids between said fibers and pigments, whereby said group member is capable of absorbing polymerizable liquid to join elements of said group member together, said vinyl siloxane groups on the surface of said group members being different from the body of said group members.

15. A method of forming a composite article which comprises wetting an inorganic solid with an olefinic polymerizable liquid capable of setting to the solid state, and allowing said liquid in contact with said solid to solidify, said inorganic solid normally having hydroxyl groups on the surface thereof but being modified by having attached to the surface thereof vinyl siloxane portions of hydrolysis products of a vinyl halosilane having only vinyl and halogen groups attached to silicon, the vinyl group being attached through a silicon-oxygen linkage.

16. An inorganic solid normally having hydroxyl groups on the surface thereof, but being modified by having attached to surface portions thereof a vinyl siloxane portion of hydrolysis products of a hydrolyzable, vinyl silane having only vinyl and hydrolyzable groups attached to the silicon atom thereof, said solid being suitable for contact with a polymerizable material to be bonded thereto, said vinyl groups being held to said surface through a silicon-oxygen linkage.

17. A method of preparing composite articles which comprises bonding vinyl-silicon-oxide groups

$$(CH_2{=}CH{-}\overset{|}{Si}{-}O{-})$$

directly to the surface of textile fibres having hydroxyl groups on the surface by contacting said fibres with a hydroxyl-reactive vinyl silicon compound having a vinyl group attached directly to silicon, thereafter contacting the said fibres with a liquid polymerizable to the solid state and comprising a styrene and polymerizing said liquid to the solid state in contact with the surface of said fibres, whereby said vinyl groups are subject to interpolymerization with polymerizable constituents of said liquid to chemically bond the insitu formed solid polymer to the surface of said textile fibres through the silicon-oxide linkage of said vinyl silicon oxide groups.

18. A method of making fibre reinforced articles which comprises wetting, with a polymerizable olefinically-unsaturated liquid capable of being solidified to the rigid state by polymerization, textile fibres, which normally have hydroxyl groups on their surfaces but which are modified by having bonded to the surface thereof a vinyl siloxane coupling compound having a carbon of an olefinic group thereof attached directly to a silicon atom, said surface of said fibres having said coupling compound thereon being different from the body of said fibres and forming an interface for interpolymerization with unsaturated groups of an olefinically-unsaturated monomeric liquid polymerizable to the solid state by means of said olefinically-unsaturated groups, and maintaining said olefinically-unsaturated liquid in contact with said fibres until it has solidified to the solid nonflowable state, the vinyl group of said vinyl siloxane coupling compound being attached through a siloxane group to said fibres, whereby said olefinic groups on the surface of said fibres are available for interaction with the monomer when it is polymerized to the solid state.

19. A method of making fibre reinforced articles which comprises wetting, with a polymerizable olefinically-unsaturated liquid which is capable of solidification to the rigid state by additional polymerization at olefine groups thereof, textile fibres, which normally have hydroxyl groups on their surfaces but which are modified by having vinyl groups with a carbon atom of the carbon-to-carbon double bond thereof chemically bonded to the surfaces thereof directly through a silicon-oxygen linkage to form an interface which is different from the body of said fibres and which may be reacted with unsaturated groups of an olefinically-unsaturated liquid polymerizable to the solid state by means of polymerization of olefinically-unsaturated groups, and maintaining said olefinically-unsaturated liquid in contact with said fibres until it solidifies to the nonflowable state, whereby said fibres become bound to the resultant polymer through interaction of said olefinic groups on the surfaces of said fibres and said unsaturated liquid during the polymerization thereof to the solid state.

20. A method of making fibre reinforced articles which comprises wetting, with a polymerizable olefinically-unsaturated liquid which is capable of solidification to the rigid state by addition polymerization at olefine groups thereof, textile fibres, which normally have hydroxyl groups on their surfaces but which are modified by having chlorvinyl groups chemically bonded to the surfaces thereof through a silicon-oxygen linkage to form an interface which is different from the body of said fibres and which may be reacted with unsaturated groups of a polymerizable olefinically-unsaturated liquid solidifiable to the solid state by means of polymerization of said olefinically-unsaturated groups, and polymerizing said olefinically-unsaturated liquid in contact with said fibres to the solid state, a carbon atom of said chlorvinyl groups being directly attached to silicon of said silicon-oxygen linkage, whereby said fibres become bound to the resultant polymer through interaction of said chlorvinyl groups on the surfaces of said fibres and said olefinically-unsaturated liquid during the polymerization thereof to the solid state.

21. A method of preparing composite articles which comprises bonding vinyl-silicon-oxide groups

$$(CH_2{=}CH{-}\overset{|}{Si}{-}O{-})$$

directly to the surface of textile fibres having hydroxyl groups on the surface thereof by contacting said fibres with a vinyl silicon halide and thereafter contacting the said fibres with a liquid polymerizable to the solid state and comprising a styrene and polymerizing polymerizable ingredients of said liquid sufficiently to solidify said liquid to a solid state while in contact with the surface of said fibres, whereby said vinyl groups on the surface of said fibres are subject to interpolymerization with polymerizable constituents of said liquid to chemically bond the in situ formed polymer to the surface of said textile fibres through the silicon-oxide linkage of said vinyl silicon oxide groups.

22. A method of preparing composite articles which comprises bonding vinyl-silicon-oxide groups

$$(CH_2{=}CH{-}\overset{|}{Si}{-}O{-})$$

directly to the surface of textile fibres having hydroxyl groups on the surface thereof by contacting said fibres with a vinyl silicon trihalide and thereafter contacting the said fibres with a liquid polymerizable to the solid state and comprising a styrene and polymerizing polymerizable ingredients of said liquid in contact with surfaces of said fibres until said liquid solidifies, whereby said vinyl groups are subject to interpolymerization with polymerizable constituents of said liquid to chemically bond the in situ formed solid polymer to the surface of said textile fibres through the silicon-oxide linkage of said vinyl silicon oxide groups.

23. A method of preparing composite articles which comprises wetting textile fibres, which normally have hydroxyl groups on their surfaces but which have surfaces modified by having bonded directly thereto vinyl siloxane groups, with a liquid polymerizable to the solid state and comprising a styrene and maintaining contact of said liquid and surfaces of said fibres until polymerizable ingredients of said liquid have polymerized sufficiently to solidify said liquid to form a solid whereby said vinyl groups are subject to interpolymerization with polymerizable constituents of said liquid to chemically bond the

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in situ formed solid polymer to the surfaces of said textile fibres through the silicon-oxide linkage of said vinyl siloxane groups, said vinyl siloxane groups on said surface being different from the main body of said fibres and providing a coupling compound different from the mass of said solid polymer, the vinyl groups of said vinyl siloxane groups being attached to said surface through siloxane groups.

24. A composite article comprising an in situ polymerized solid polymer of a liquid comprising a polymerizable olefinic compound selected from the group consisting of diolefinic compounds having a chain of less than 7 aliphatic carbon atoms and polymerizable mono-olefinic compounds, textile fibres in said polymer for reinforcing the same and an interfacial coupling compound bonded to said textile fibres and chemically combined with said solid polymer, said interfacial compound being different both from the body of said fibres and the mass of said solid polymer, said interfacial compound comprising the interpolymerization product from the interpolymerization of vinyl siloxane groups on the surfaces of said fibres and of said olefinic compound, said vinyl groups being attached directly to silicon and being bonded to said fibres through silicon-oxygen linkages.

25. A composite article comprising an in situ polymerized solid polymer of a liquid comprising a monomeric polymerizable styrene, textile fibres for reinforcing the same, and an interface comprising a coupling compound bonded to said textile fibres and in chemical combination with said solid polymer, said interface being different both from the mass of said solid polymer and from the body of said textile fibres and comprising an interpolymer of vinyl groups which are bonded to the surfaces of said fibres through siloxane groups and said styrene.

26. A composite article comprising an in situ polymerized solid polymer of a liquid comprising a polymerizable mono-olefinic compound, textile fibres in said polymer for reinforcing the same and an interfacial coupling compound bonded to said textile fibres and in chemical combination with said solid polymer, the interface of said

polymer being different both from the body of said fibres and the mass of said solid polymer, said interfacial compound comprising an interpolymerization product of vinyl groups, which are bonded to the surfaces of said fibres through siloxane groups and said olefinic compound.

27. Textile fibres which normally have hydroxyl groups on the surface thereof modified by having chlorovinyl siloxane groups bonded to the surface thereof, the chlorovinyl groups of said chlorovinyl siloxane being attached to the surface of said fibres through siloxane groups.

28. A liquid-permeable mass of substantially dry flexible textile fibres suitable for soaking up a polymerizable liquid, said fibres being of a material which normally carries hydroxyl groups on the surface thereof, the surfaces of said fibres being modified by having groups of a vinyl siloxane attached thereto for subsequent reaction with said polymerizable liquid during the polymerization thereof, the said vinyl groups being attached through said siloxane groups to said surface, the fibres having said vinyl groups attached thereto being wettable by said polymerizable liquid, whereby said mass is capable of soaking up polymerization liquid to bond said fibres together upon the polymerization thereof and whereby a molecular bond between the surface of the fibres and the resultant polymer may be had by interaction of said vinyl groups and said polymerizable liquid during said polymerization.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,742,378 April 17, 1956

Theodore A. Te Grotenhuis

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 11, line 68, for "additional" read --addition--; column 14, line 22, for "polymerization" read --polymerizable--.

Signed and sealed this 3rd day of July 1956.

(SEAL)
Attest:
KARL H. AXLINE
Attesting Officer

ROBERT C. WATSON
Commissioner of Patents

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United States Patent Office

2,841,566

Patented July 1, 1958

2,841,566

HIGH POLYMERS WITH CHEMICALLY BONDED REINFORCING AND METHOD OF MAKING SAME

Theodore A. Te Grotenhuis, Olmsted Falls, Ohio, assignor of twenty percent to The General Tire & Rubber Company, Akron, Ohio, a corporation of Ohio

No Drawing. Original application August 2, 1952, Serial No. 302,415, now Patent No. 2,742,378, dated April 17, 1956. Divided and this application June 25, 1954, Serial No. 439,463

14 Claims. (Cl. 260—17.4)

This application is a division of my application Serial No. 302,415, filed August 2, 1952, which is a continuation-in-part of my application Serial No. 243,737, filed August 25, 1951; which is a continuation-in-part of my application Serial No. 585,824, filed March 30, 1945, which application was copending with application Ser. No. 593,970, filed May 15, 1945 (now abandoned), and with application Serial No. 559,848, filed October 31, 1944, now Patent 2,457,097, which is a continuation-in-part of application Serial No. 424,493, filed December 26, 1941, now abandoned.

The present invention relates to composite articles of reinforcing material such as pigments and fibers, preferably a matted or woven fabric, and a high molecular weight polymeric substance. It particularly relates to composite articles and methods of preparing such articles comprising a water insoluble inorganic pigment or textile fabric or fibers and in situ polymerized high polymer molecularly bonded to said fabric by interaction of unsaturated linkages on the fiber or pigment surface and of the monomer entering into the solid polymer. The term "polymer", is herein used in its generic sense to include copolymers of one or more monomers.

Composite articles of pigments such as silica, titania, carbon black, etc. and/or fibers such as cellulosic fibers, glass fibers, and the like, and a high polymer such as a polymer of a material comprising a mono-olefinic compound such as styrene, and methyl methacrylate, as a substantial polymerizing ingredient thereof are well-known. Such composite articles in which the pigments, fabric or fibers act as reinforcing agents which should contribute great strength and impact resistance to the articles sometimes have relatively low water resistance or the bond between the water insoluble pigment or fiber and the resin is insufficient to prevent rupture when contacted with certain fluids. The strength of the composite article may also be much less in the dry state than should be the case if proper adhesion of fiber and polymer were obtained. Even thermoset or cross-linked polymers reinforced with fibers and pigments are frequently adversely affected. The result is to limit the utility of the composite article.

It is an object of the present invention to provide reinforced articles of any textile fabric and a high polymeric material formed of a monomer having polymerizable olefinic unsaturation, in which the bond between the fabric and the high polymer may be chemical in nature and therefore much stronger than the usual adhesive forces.

It is another object of the present invention to provide a textile fabric which, when treated with free radical polymerized mono-olefinic monomers or mixtures comprising such monomers can form interlocking chemical bonds therewith.

It is another object of the present invention to provide a method of treating fine particles such as pigments, fibers, and fabrics so that they are readily compounded with organic substances and so that they can be bonded thereto by chemical means such as by possible interpolymerization or by sulfur or chemical bridges.

It is another object of the present invention to provide a method of treatment for fine particles and fibers by which the particles are rendered more readily wettable and interlocked with polymerizable organic compounds and polymers.

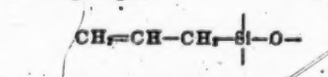
It is still another object of the present invention to provide a simple and inexpensive method of improving the ease of dispersion and compounding of fine particles in organic vehicles and polymers.

It is a further object to provide composite articles and a method of making composite articles comprising a solid polymer of a free radical polymerizable unsaturated material reinforced with textile fabric and having the textile fabric molecularly interlocked with said solid polymer. Other objects will be apparent from the following description of the invention.

In accordance with the present invention, and as described in my aforementioned copending application Serial No. 585,824, an alkenyl silicon halide having up to twenty carbon atoms in an organic group is deposited on the surface of the fabric or pulverulent solid. This is most conveniently accomplished by subjecting the surface of the fabric to contact with a reactive organosilicon compound containing at least one allyl group, which is of course characterized by having an olefinic group spaced by a carbon atom from the silicon which carries it, at least one group split off together with H from contacting —OH to form a new silicon-oxygen bond. The preferred organo silicon compounds have the general formula

where X is a group which split off with hydrogen from contacting hydroxyl groups with formation of a new silicon-oxygen bond. X is preferably chlorine or bromine, although it may be oxyaryl, oxyaliphatic, or amino (NH_2 groups), and Y and Z may be selected from any monovalent organic groups, preferably those hydrocarbons with less than 7 carbon atoms such as allyl, vinyl, phenyl, methyl, etc., and groups split off by reaction with hydroxyl groups and oxgen-containing groups.

This treatment provides on the surface of the fibers the allyl siloxane groups



where the free silicon valences are attached to oxygen or carbon and the free oxygen valence is generally attached to the surface of the fiber or pigment. Those compounds having a carbon-to-silicon bond are preferred because of their increased stability at elevated temperatures.

Examples of suitable hydroxyl or water-reactive, aliphatically unsaturated organosilicon compounds are those set forth in my aforementioned copending application Serial No. 585,824, now Patent No. 2,751,369, and especially those having allyl groups for interaction with in situ free radial polymerizable monomer containing compositions such as the water hydrolyzable allyl silicon halides including the mono-, di-, and tri-allyl silicon chlorides, bromides, and amines, the halo-allyl silicon chlorides and bromides such as the chlorallyl silicon chlorides. If more than one organic group is attached to silicon, only one need be an allyl group to enter into the copolymerization with the monomer. Thus, the allyl methyl silicon dichlorides are suitable. Even the partially condensed (liquid) siloxanes appear to be water hydrolyzable or re-

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active to hydroxyl to shift oxygen and form a new silicon-oxygen bond to the surface of the pigment or fiber.

Although the present invention is not concerned with the preparation of the allyl silicon compounds per se, the organo-silicon compounds which contain a group which is split off by reaction with water because of extreme desire of silicon to form a new silicon-oxygen bond and which contains an allyl group attached to the silicon atom may be prepared in any suitable way as by one or more of the previously proposed methods, for example, the Grignard synthesis wherein the desired organo-halide as for example allyl bromide is reacted with silicon tetrachloride of a mono- or di-organo substituted silicon tetrachloride in the presence of magnesium, etc. The conditions for Grignard reactions are well known in the art.

The preparation or properties of organo-substituted silicon halides (organohalo silicones) is well known and is set forth in one or more of the following United States patents:

Lincoln et al.— 2,129,281
Nason— 2,182,208
Rochow— 2,258,218–19–20–21–22
Rochow—2,286,763
Rochow— 2,352,974
Hyde— 2,371,050
Rochow— 2,371,068

The reinforcing such as the pigment, textile fabric, or other fibrous material used as reinforcing in the composite articles formed in accordance with the present invention may be treated simply by contacting the dry fabric with the hydroxyl water hydrolyzable or condensable silicon compound such as the allyl silicon chlorides or allyl silicon amines, etc. Any method of effecting contact either vapor phase or liquid may be used. The one or more of the reactive silicon compounds (at least those which are relatively non-volatile) are preferably admixed in solution in a non-reactive solvent such for example as a hydrocarbon liquid such as benzene, toluene, or any other diluent that does not react with the silicon halides or amine used. The silicon compound is preferably present in small proportions in the solvent such as .1% to 5% although the reactivity of silicon is such that the extremely dilute solutions are effective. When the silicon compound is liquid, the substantially pure liquid may be used, although a dilute solution is more desirable. The reactive silicon compound apparently reacts with hydroxyl or carboxyl groups chemically absorbed or combined with the surface of the fabric to bond allyl groups to the surface thereof through silicon atoms. Such groups are highly compatible with olefinic polymerizable materials and are capable of chemically combining into the molecules formed by the polymerization of such materials. The fibers, fabrics and pigments treated with the solution should be dry and free from water so that reaction with water and hydroxyl not chemically combined or held on the surface of the fibers is avoided. The treated fabric may be neutralized, heated, or washed to eliminate or vaporize traces of acid or ammonia alcohol, etc. or these materials may be volatilized therefrom.

In accordance with the present invention, the fabric or pulverulent inorganic solid which has been treated as above is contacted or immersed in a composition comprising a polymerizable olefinic compound, such as that described in my aforesaid application Serial No. 302,415, now Patent No. 2,742,378, and in my application Serial No. 585,824, now Patent No. 2,751,369, from which the subject matter of this application has been divided. The olefinic compound is preferably a polymerizable styrene or methyl methacrylate which contains conjugated double bonds and containing a free radical initiator such for example as a peroxide and hydroperoxide catalyst, and the polymerizable mono-olefinic compound is subjected to

catalyst and caused to polymerize and thus cause the composition to set to the solid state while in contact with the treated fabric whereby interaction of double bonds on fabric and monomer occur to build the fabric chemically into the solid molecule. The mono-olefinic monomer (a styrene or methyl methacrylate) may contain other ingredients such as a polyester, such as the condensation product of a glycol, maleic anhydride and phthalic anhyride, and diallyl phthalate, etc. or polystyrene, etc., dissolved therein to interpolymerize or to interact with the styrene and/or methyl methacrylate in forming the solid polymer. When a solution in the monomeric polymerizable material (for example the styrene and/or methyl methacrylate) of a resinous polymer such for example as polystyrene, polymethyl methacrylate, polymethyl acrylate, or other organic polymerization or condensation product is applied to the surface of the treated fabric or pulverulent solid and the solvent caused to polymerize in situ a more adherent coating may be had to the fabric and a direct chemical union between the fibrous material and the polymerizable or dissolved constituents is usually obtained.

Examples of the most commonly used free radical initiators or catalysts are benzoyl peroxide, cumene hydroperoxide, tertiary butyl hydroperoxide, and other organic peroxides and hydroperoxides. The peroxide, as is well known, is usually used in relatively small amounts such as 1 to 2% of the weight of the polymerizable ingredient, such for example as the monomeric styrene present. Any of the various free radical initiators may be used when soluble or usable in one of the liquids of the method of polymerization used.

The temperature of polymerization is generally dependent on the size of the articles produced and the amount of catalyst present, it being necessary to remove the heat of polymerization. Higher temperatures increase polymerization speed, and cause greater exothermic reaction and may be used in thinner and smaller articles. The polymerization temperature is usually within the range of 50° F. to 200° F. and should be well below the boiling point of monomers present at the pressure used.

The following examples illustrate the present invention.

Example 1

A dry, glass fabric which has been previously freed from sizing and dried at 100° C. in a vacuum oven is submerged in a solution in 100 parts of dry toluene of five parts of a mixture of vinyl silicon chlorides having one to three vinyl groups attached directly to silicon and the remaining valences attached to chlorine. The fabric is allowed to stand in the solution for a few minutes, removed and drained free of liquid, and dried in a 75° C. vacuum oven to remove all traces of hydrochloric acid. The thus treated fabric is thereupon immersed into a styrene solution comprising 60 parts of styrene and 40 parts of a polyester prepared by condensing about 30 mol parts of maleic anhydride with 70 mol parts of adipic acid and 102 mol parts of ethylene glycol until a relatively viscous material is obtained, boiling at least 250° C. In effecting the condensation, the ingredients are heated slowly at first under an inert gaseous atmosphere, for example N_2, CO_2 etc., and the amount of heat applied is merely sufficient to cause vigorous boiling. As the reaction progresses, with elimination of water the temperature rises, until a temperature of about 250° C. is obtained. The styrene solution of the polyester is mixed with one part of cumene hydroperoxide as a free radical initiating catalyst and is maintained at slightly elevated temperatures under an atmosphere of nitrogen and with oxygen excluded until a hard solid article is produced having the fabric in situ and intimately bonded through the now polymerized unsaturated linkages to the solid copolymer thus obtained.

Example 2

When several sheets of fabric are wetted as in Example 1 with the solution of unsaturated polyester in styrene and the wetted sheets piled up and pressed against each other and allowed to so remain until the polymerization progressed to the solid state, a laminated structure having exceptionally desirable properties is obtained.

Example 3

In place of the polyester-styrene solution of Example 1, a solution of polystyrene in styrene monomer and having about the same viscosity is substituted, other conditions being the same. An article having fabric bonded to the in situ polymerized polymer is also obtained.

Example 4

The styrene polyester solution of Example 1 is substituted by a viscous solution of polymethylmethacrylate in methacrylate monomer and the polymer, monomer, fiber mixture thus obtained is allowed to polymerize in shape form as in Example 1, except that the temperature was raised to about 80° C. and the catalyst was substituted by 1% based on the weight of the monomer present of benzoyl peroxide, other conditions being the same. A shaped article having fabric or fiber intimately bonded in situ is also obtained.

The vinyl silicon halides in the above examples may be substituted by allyl silicon halides to also produce an integrally bonded composite article having excellent properties. The glass fabric may be substituted for matted glass fibers and other textile fabrics including cotton, rayon, and the like having oxygen containing hydroxyl groups (which of course are present in carboxyl groups) on surface portions thereof, the fabric or fibers in each instance being bonded to the in situ polymerized polymer by interaction of the unsaturated groups and the surface thereof with the monomer during the polymerization thereof. The solution containing the polymerizable monomer of the above examples may be substituted by other monomers or mixtures comprising monomers polymerizable as by homopolymerization, copolymerization, or interpolymerization to the solid state by free radical mechanism.

Example 5

100 grams of unbeaded carbon black are subjected to agitation in the presence of about one gram of a saturated vapor of a mixture of allyl dimethylsilicon chloride and methyl diallylsilicon chloride, the presence of saturated vapor being insured by a reducing of the pressure and elevating the temperature in the container. The agitation is continued in the presence of the organosilicon halide vapor for about 10 minutes to allow thorough penetration of the vapor through the carbon black. The hydrochloric acid formed by the faction is removed in any suitable manner, as for example vaporization at elevated temperature by neutralizing with an alkali material such as dry NH_3, by shaking the carbon black with water, or preferably by treating the carbon black with ether and water and washing the carbon black-ether mix until free from acid. The carbon black thus treated has much less tendency to be wet by water and much greater tendency to be wet by hydrocarbon organic solvents and contains allyl groups attached thereto for interpolymerization with free radical polymerizable materials, such as diallyl phthalate and the like.

The pigments in the above example may be substituted by other finely divided pigments including silica, aluminum oxide, titanium oxide, and the like, as well as fibers. Monomers such as styrenes (including styrene, vinyl toluene, etc.), methyl methacrylate, butadiene, and the like are characterized by having a double bond in conjugated relation with the polymerizable olefinic double bond for resonant activation thereof. As described in my said application Serial No. 589,824 and particularly Example 7 of the said patent issued thereon rubbers including "GRS," natural, "Butyl" and neoprene or their vulcanizing agents also react with the said olefinic groups of the siloxane on pigment particles to form a chemical bond.

Other pigments and fibers including glass fiber, rayon, cotton, and cellulose fibers having the siloxane units attached to their surface as above noted may be substituted for those of above examples.

The term "polymerization" is here used and in the appended claims in the usual generic sense to include copolymerization. Similarly the term "polymer" is used in the usual sense to include copolymers whether of the olefine-reactive addition type or of the olefine-reactive condensation type. The terms "pulverulent inorganic solids and pigments" are used in their broadest sense to include inorganic pigments, inorganic powders and inorganic pulverizable solids, regardless of coloring value.

It is to be understood that in accordance with the provisions of the patent statutes, variations and modifications of the specific examples herein described for purposes of illustration may be made without departing from the spirit of the invention.

What I claim is:

1. A method of forming a composite article comprising a mass of a member of the group consisting of inorganic pulverulent solids and fibers bonded to a resinous polymer polymerized in situ to the solid state which comprises wetting said group member with a polymerizable liquid in a continuous phase and comprising a monomeric polymerizable styrene and without agitation causing polymerization of said monomeric styrene in contact with said group member and in a continuous phase, said group member being characterized by having attached to surface portions thereof a coupling compound comprising an allyl siloxane group, the body of said group member and the body of said resinous polymer being different.

2. A method of forming a shaped composite article comprising a member of the group consisting of fibers and pulverulent inorganic solids bonded together in a mass through a solid polymer of a liquid comprising an olefinic compound having at least one pair of olefinic double bonds in conjugation with another pair of bonds, whereby said olefinic double bonds are activated toward polymerization, said polymer being in situ polymerized to the solid state, said method comprising wetting said surfaces with said liquid having said olefinic compound in a continuous phase and having in admixture therewith a free radical forming polymerization catalyst maintaining said liquid in contact with said surfaces and in a continuous phase until it is solidified to the solid state, agitation being absent during change of said liquid from the flowable to the solid state, said surfaces being characterized by having attached thereto a coupling compound comprising an allyl siloxane group, the body of said solids having said surfaces and the body of said solid polymer being different both from said coupling compound and from each other.

3. The method of claim 2 wherein said olefinic compound is methyl methacrylate.

4. A method of bonding textile fibers having hydroxyl groups on their surfaces to a polymer of a liquid comprising a styrene which comprises reacting said hydroxyl groups on the surface of said fibers with a hydroxy reactive allyl silicon compound having an allyl group directly attached to silicon and a hydroxyl reactive group directly attached to silicon to bond allyl siloxane groups to the surface of said fibers, thereafter contacting the surface of said fibers with a liquid mixture polymerizable to the solid state and comprising a styrene in a continuous phase and polymerizing said liquid while in the continuous phase to the solid state in contact with the

surface of said fibers, the solidification of said liquid occurring without agitation, whereby said allyl groups are subject to interpolymerization with polymerizable constituents of said liquids to chemically bond the in situ formed solid polymer to the surface of said textile fibers through the silicon-oxygen linkages of said allyl siloxane groups.

5. A composite article comprising an in situ polymerized solid polymer of a liquid comprising an olefinic compound with conjugated double bonds in a continuous phase, textile fibers in contact with said solid polymer and an interfacial coupling compound bonded to said textile fibers and to said solid polymer, said interfacial compound being different both from the body of said fibers and the mass of said solid polymer, said interfacial compound comprising the product from the polymerization of said olefinic compound in contact with the allyl siloxane groups on the surface of said fibers, said allyl groups being attached directly to silicon and being bonded to said fibers through silicon oxygen linkages.

6. A composite article comprising an in situ polymerized solid polymer of a liquid comprising a monomeric polymerizable styrene in a continuous phase; textile fibers for reinforcing the same and an interfacial coupling compound bonded to said textile fibers and in chemical combination with said solid polymer, said interface being different from both the mass of said solid polymer and from the body of said textile fibers and comprising a product of the interpolymerization of said styrene with allyl groups of allyl siloxane groups bonded to the surface of said fibers.

7. A composite article comprising an in situ polymerized solid polymer of a liquid comprising a monomeric polymerizable methyl methacrylate in a continuous phase, textile fibers for reinforcing the same and an interface comprising a coupling compound bonded to said textile fibers and in chemical combination with said solid polymer, said interface being different from both the mass of said solid polymer and from the body of said textile fibers and comprising a product of the interpolymerization of said methyl methacrylate with allyl siloxane groups on the surfaces of said fibers.

8. A method of forming a composite article comprising inorganic surfaces bonded together through an in situ formed solid polymer of a liquid comprising a monoolefinic compound having olefinic double bonds conjugated with double bonds, said method comprising wetting said surfaces with said liquid having said monoolefinic compound in a continuous phase and having in admixture therewith a free radical forming polymerization catalyst maintaining a mass of said liquid as a continuous phase in contact with said surfaces without agitation until it is solidified to the solid state to bond said surfaces together, said surfaces being characterized by having attached thereto a coupling compound comprising an olefinically unsaturated organosiloxane group in which carbon-to-carbon double bonds are spaced by at least one carbon atom from the silicon atom carrying the organic group of said organosiloxane group, the body of said solids having said surfaces and the body of said solid polymer being different both from said coupling compound and from each other, said olefinically unsaturated group being an alkylenyl group having not over twenty carbon atoms.

9. A composite article comprising an in situ polymerized solid polymer of a liquid comprising an olefinic compound in a continuous phase with conjugated double bonds, textile fibers in contact with said solid polymer and an interfacial coupling compound of not more than twenty carbon atoms in an alkylenyl group bonded to said textile fibers and to said solid polymer, said interfacial compound being different both from the body of said fibers and the mass of said solid polymer, said interfacial compound comprising the product from the polymerization of said olefinic compound in contact with an olefinically unsaturated organosiloxane group which has olefinic unsaturation in which carbon-to-carbon double bonds are spaced by one, and only one carbon atom from the silicon atom carrying the organic group of said organosiloxane group on the surface of said fibers, said groups being attached directly to silicon and being bonded to said fibers through silicon-oxygen linkages.

10. A composite article comprising a mass of nonfibrous inorganic solid particles bonded together through a continuous phase of solid polymer of a continuous phase of olefinic-reactive polymerized liquid in situ polymerized to the solid state, said particles having an interfacial coupling compound bonded to the surface thereof and chemically bonded to a continuous phase of said in situ solidified solid polymer, said interfacial compound being different from both the body of said inorganic solid particles and from the mass of said solid polymer uniting said inorganic solid particles together, and comprising the reaction product of said solid polymer during the solidification thereof with

$$CH_2{=}CH{-}C{-}Si{-}O{-}$$

groups on the surface of said inorganic solid particles, where the silicon is connected directly only to a member of the group consisting of hydrocarbon groups and oxygen and the silicon-oxygen linkage bonds the hydrocarbon groups to the surface of said pulverulent inorganic solid particles.

11. A composite article comprising a binder of an in situ polymerized solid resinous polymer of an olefinic compound having at least one pair of olefinic double bonds in conjugation with another pair of double bonds, a member of the group consisting of textile fibers and pulverulent inorganic solids in said polymer and bound together by in situ polymerization of said polymer, and an interfacial coupling compound bonded to said group member and chemically combined by in situ interpolymerization of said olefinic compound while in a continuous phase and in contact with said coupling compound, said interfacial compound being different from both the body of said group members and the mass of said solid polymer, said interfacial compound comprising the product resulting from the polymerization of said olefinic liquid in contact with allyl siloxane groups on the surface of said group member, said allyl groups of said allyl siloxane groups being bonded to said group member through silicon-oxygen linkages.

12. An article according to claim 11 wherein said olefinic compound is styrene and wherein an inorganic powder is bonded to the polymerization product thereof.

13. An article according to claim 11 wherein said olefinic compound is styrene.

14. An article according to claim 11 wherein said olefinic compound is methyl methacrylate.

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